A New Model for the Full Inclusion of Precipitation Reactions in the General Ionic Equilibrium Framework of Homogeneous Solutions Based on the Fraction of Species Concept in Heterogeneous Systems

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Abstract: This study aims at extending the general methodology for the study of predominance and reactivity of ionic homogeneous solutions to precipitation reactions. This extension was satisfactorily formulated by the definition of the fraction of species concept in heterogeneous systems for the first time. An easy form to fully integrate the ion product concept with other descriptions of homogeneous ionic reactions, to obtain predominance zone diagrams (PDZ), to enrich the use logarithmic relative diagrams, to generate continuous equations from titration curves, and to generalize side-reaction coefficients to heterogeneous systems using easy-to-compute algorithms of calculation is shown.

The new representation was applied in a study case exemplified by the hydrolysis of copper (II) in the absence and the presence of complexing ligands considering soluble and insoluble species of the metal ion. The results perfectly compare to those obtained by established numerical and graphical methods of analysis of solution equilibria showing the equivalence among the different descriptions.

Pre-nucleation clusters (PNCs) theory of precipitation reactions was used as a mean to interpret the theoretical implication that this view engendered.

Keywords: Distribution fraction diagram, predominance zone diagram, precipitation reactions, side-reaction coefficients, modeling precipitation reactions.

1. INTRODUCTION

The object of analytical chemistry is to obtain qualitative and quantitative information about the chemical composition and structure of materials. Analytical chemistry investigates the type of components present in materials, their amount, and their structural relationships [1]. From the analytical chemistry point of view, the structure of aqueous solutions of ions and neutral molecules is related to the inner relationships that the different species establish among them due to fundamental chemical principles, such as the conservation of matter and charge, and the thermodynamic equilibrium. Basic theory of solution chemistry is essential to study the physicochemical phenomena that are applied in chemical analysis, allowing the understanding of sample pretreatment and preparation methods used in conjunction with modern instrumental techniques. The importance of accurate sample preparation techniques cannot be overstated, as even the best analytical techniques cannot rectify problems generated by sloppy sample pretreatment [2].

With the extended use of analytical methods among different chemical and non-chemical related disciplines, there is an increasing need to conceptualize the principles of solution chemistry in such a form that problem descriptions are simplified, common methodologies to plan and resolve complex problems of analytical and industrial chemistry can be employed, and non-expert users of analytical methods can have an easy comprehension of the rules lying behind the use of diverse chemical operations in aqueous solutions (pH buffering, use of masking and precipitating reagents, control of redox potential, etc.).

On this subject, general approaches to include in a single scheme homogeneous ionic reaction, e.g., acid/base, complex, and redox systems, have been proposed as an appropriate conceptual framework from which the composition and reactivity of complex ionic media can systematically be analyze [3-6]. One of the great interests in the analytical chemistry practiced in aqueous solutions lies in the fact that it can be quasi-systematically described by mathematical equations, which can be grouped themselves in mathematical determined systems [7]. Consequently, the arithmetic structures of such systems and methods for the treatment of solution equilibria by different approaches have been reported over time [7-9]. With the availability of personal computers with spreadsheet and mathematical software, various computer methods and graphical approaches based on the concept of master variables can be now easily implemented [10-13]. Such approaches use the concepts of “particle exchange” and “distribution or fraction diagrams” as fundamental starting points from which predominance-zone diagrams (PZD) can be constructed and reactivity of a system deduced [3, 14-17]. However, as for precipitation reactions is concerned, they have generally been treated separately from this general framework. There are at least two probably reasons for this: the intrinsic heterogeneous character of the reaction that leads to a phase separation phenomenon, and the absence of a linking frame from which different approaches to study such reactions can be integrated. As for the second reason, it is reasonable to think that if, ultimately,
precipitation reactions are complexation ones with the characteristic that the complex is in a sparingly soluble form, it should be possible to treat them as such with some particularity. In this regard, Fernández-Pereira et al. [18] based on the concept of acceptance potential has established a correlation of the precipitation-solubility equilibrium with other ionic equilibria; however, the theoretical implication of such inclusion and a complete view of the panorama of all the possibilities allowed by such incorporation have not been deeply examined up to now. In this work, it will be shown that the possibility to include precipitations reactions in the general ionic equilibrium framework of homogeneous reactions just requires an appropriate definition of the fraction of species concept in the heterogeneous system using a modified equilibrium constant value. It is the intention of the manuscript to shed light upon the advantages of such approach to simplify the description of precipitation reactions based on previous knowledge of homogeneous ionic reactions and to promote critical reflection about the implications of such view.

In a first instance, and for the sake of clarity in the presentation, preliminary concepts in solution chemistry exemplified with acid/base reactions will be reviewed; then, the generalization of the homogeneous framework to include precipitation reactions will be formally introduced. To show the feasibility and applicability of the approach, the results of the use of the proposed methodology to analyze the composition of a complex heterogeneous system will be compared to that obtained by established numerical methods. Furthermore, it will be shown how an established graphical method can take advantage of the new approach to enrich its range of application by obtaining easily PDZ diagrams in heterogeneous systems. Finally, titration curves for precipitation reactions will be computed using the framework commonly used for homogeneous reactions, and the generalization of side-reaction coefficients [19, 20] to heterogeneous systems will be performed in a straightforward form. Overall, the integration of precipitation reactions in the homogeneous equilibrium framework will then be demonstrated and its applications and implications in the chemical descriptions of solution chemistry problems properly analyzed.

2. THEORETICAL BASIS

Review of the general ionic equilibrium framework of homogeneous solutions as applied to acid/base reactions

HA/A− system

As an illustrative example well found in the literature [4, 21, 22], considering the proton exchange between a donor (acid, HA) and an acceptor (base, A−) species of this particle according to the reaction:

\[ HA + H_2O \leftrightarrow A^- + H_3O^+ \]  

(1)

the mole fraction of both species in a system with total concentration \( C_{HA} \) may be computed from:\n
\[ x_{HA} = \frac{[HA]}{C_{HA}} \quad \text{and} \quad x_{A^-} = \frac{[A^-]}{C_{HA}} \]  

(2)

Where

\[ C_{HA} = [HA] + [A^-] \]  

(3)

Using the acid equilibrium constant, \( K_a \), under ideal conditions, i.e., the activities of the species correspond to their concentrations, defined by:

\[ K_a = \frac{[A^-][H^+]}{[HA]} \]  

(4)

And the mass balance (Eq. (3)), \( x_{HA} \) and \( x_{A^-} \) are expressed as:

\[ x_{A^-} = \frac{[A^-]}{[HA] + [A^-]} = \frac{K_a}{K_a + K_{eq}} = \frac{10^{-pK_a}}{10^{-pH} + 10^{-pK_a}} = 1 - x_{HA} \]  

(5)

\[ x_{HA} = \frac{[HA]}{[HA] + [A^-]} = \frac{1}{K_a + K_{eq}} = \frac{10^{-pH}}{10^{-pH} + 10^{-pK_a}} = 1 - x_{A^-} \]  

(6)

taking into account that \( pH = -\log[H^+] \) and \( pK_a = -\log K_a \).

From Figure 1a it is clearly noted that when \( [H^+] > K_a \), \( pH < pK_a \), \( x_{HA} > x_{A^-} \), and when \( [H^+] < K_a \), \( pH > pK_a \), \( x_{HA} < x_{A^-} \); clearly at \( [H^+] = K_a \), \( pH = pK_a \), \( x_{HA} = x_{A^-} \). From the same Figure, it is observed that in a rigorous sense both species, the acid and the base, are simultaneously present within all pH range; however, its relative abundance or predominance is determined by the conditions indicated before.

It is possible to demonstrate that the same information may be attained using logarithmic diagrams without the need of computing the fraction of species as described above, as this alternative representation just requires performing pertinent approximations to the equilibrium relationship (Eq. (4)) and the mass balance condition (Eq. (3)) to get lineal relationships that can be easily drawn [4, 22-25]. Accordingly, when \( pH < pK_a \), \( [HA] \gg [A^-] \) and \( [HA] \approx C_{HA} \) and two lineal forms, one for each species can be deduced:

\[ \log[HA] = \log C_{HA} \]  

(7)

\[ \log[A^-] = -pK_a + \log C_{HA} + pH \]  

(8)

Similarly, when \( pH > pK_a \), \( [HA] \ll [A^-] \) and \( [A^-] \approx C_{HA} \) and

\[ \log[A^-] = \log C_{HA} \]  

(9)

1Mole fractions have been represented with different symbols in the literature, mainly \( x_i \). In the following, it was decided to employ \( x \) to avoid a confusion with the \( a_i \) symbol employed for side-reactions coefficients and to be consistent with most physicochemical textbooks.
log [HA] = pK_a + log C_{HA} - pH  

(10)

To perform a comparison between both procedures Eqs. (2) are transformed to their logarithms forms to get:

log [HA] = log C_{HA} + log x_{HA}  

(11)

log [A^-] = log C_{HA} + log x_{A^-}  

(12)

In Figure 1b, created using Excel, it is seen that the horizontal line at log C_{HA} = log [HA] or log [A^-] is a graphic representation of the mass balance condition (Eq. (3)), and the equilibrium condition (Eq. (4)) is represented by the two straight lines given by Eqs. (8) and (10).

In Figure 1b both procedures are compared as well. As observed, the main difference arises from the nature of the approximation done when drawing the lineal equations, as strictly speaking, at the system point pH = pK_a neither species can be neglected in the mass balance condition, where [HA] = [A^-] = C_{HA}/2. So it is found that the true curves for HA and A^- in the lineal logarithmic equations must intersect at pH = pK_a but 0.3 units (log 0.5) below the mass balance line, as obtained using Eqs. (11) and (12) which do not use any approximation.

The PZD (Figure 1c) visually simplifies the x_i = f(pH) diagram in a unidimensional representation such that the more abundant species in each pH region is easily identified considering that in the coexistence line pH = pK_a both species have the same relative abundance. From this scale, the reactivity of an acid/base system is easily deduced considering that acid/base species can coexist in pH regions that agree with their predominance zone, otherwise species should be transformed by particle exchange to meet this requirement [17].

Alternatively, Eqs. (5) and (6) may be expressed in terms of the global stability constant of the system defined by:

\[ \beta_1 = \frac{[HA]}{[A^-][H^+]} \]  

(13)

as:

\[ x_{A^-} = \frac{[A^-]}{C_{HA}} = \frac{[A^-]}{\beta_1[H^+][HA][A^-]} = \frac{1}{1 + \beta_1[H^+]} \]  

(14)

\[ x_{HA} = \frac{[HA]}{C_{HA}} = \frac{\beta_1[H^+]}{1 + \beta_1[H^+]} = 1 - x_{A^-} \]  

(15)

Although such constants are scarcely employed in the literature concerning acid/base reactions the advantage of its use will be shown subsequently.

**H_A/A^{n-} system**

For a polyprotic system of the type

\[ HA^{(n-1)^-} \leftrightarrow A^{n^-} + H^+ \]  

\[ K_{a1} = \frac{[A^{n^-}][H^+]}{[HA^{(n-1)^-}]} \]  

(16)

allow to easily formulate the fractions of species equations as:

\[ H_2A^{(n-2)^-} \leftrightarrow HA^{(n-1)^-} + H^+ \]  

\[ K_{a2} = \frac{[HA^{(n-1)^-}][H^+]}{[H_2A^{(n-2)^-}]} \]  

(17)

\[ H_nA \leftrightarrow H_{n-1}A^- + H^+ \]  

\[ K_{an} = \frac{[H_{n-1}A^-][H^+]}{[H_nA]} \]  

(18)

The corresponding \( \beta_i \) expressions:

\[ \beta_1 = \frac{1}{k_{a1}} = \frac{[HA^{(n-1)^-}]}{[A^{n^-}][H^+]} \]  

(19)

\[ \beta_2 = \frac{1}{k_{a1}k_{a2}} = \frac{[H_2A^{(n-2)^-}]}{[A^{n^-}][H^+]^2} \]  

(20)

\[ \beta_n = \frac{1}{k_{a1}k_{a2}\cdots k_{an}} = \frac{[H_nA]}{[A^{n^-}][H^+]^n} \]  

(21)
\[ x_{An^-} = \frac{[A^{n-}]}{C_{HA}} = \frac{[A^{n-}] + [H_2A^{(n-2)}] + \ldots + [H_nA]}{1 + \beta_1[H^+] + \beta_2[H^+]^2 + \ldots + \beta_n[H^+]^n} \]  
\tag{22}

\[ x_{HA^{(n-1)-}} = \frac{[HA^{(n-1)-}]}{C_{HA}} = \frac{[A^{n-}][HA^{(n-1)-}]}{[A^{n-}]C_{HA}[A^{n-}]} = x_{An^-}\beta_1[H^+] \]  
\tag{23}

\[ x_{H_2A^{(n-2)-}} = \frac{[H_2A^{(n-2)-}]}{C_{HA}} = \frac{[A^{n-}][H_2A^{(n-2)-}]}{[A^{n-}]C_{HA}[A^{n-}]} = x_{An^-}\beta_2[H^+]^2 \]  
\tag{24}

\[ x_{H_nA} = \frac{[H_nA]}{C_{HA}} = x_{An^-}\beta_n[H^+]^n \]  
\tag{25}

Moreover, as these expressions have a general character, they can be applied for the exchange of other particles different from \( H^+ \). The utility of this formulation will be appreciated later when analyzing the simultaneous participation of \( OH^- \) particles in precipitation and complexation equilibria.

The above framework can be applied to redox (through the incorporation of the \( \varphi \) or \( pE = -\log[e^-] \) and \( \varphi_{\text{red}} \) or \( pE^0 = -\log K_{\text{red}} \) concepts) and complex equilibria as well. This straightforward generalization of acid/base, complex, and redox ionic systems can be applied to homogeneous ionic reactions. The concentration that is in the soluble form, as expected. As for the chemical equilibrium:

\[ MX \leftrightarrow \text{M}^+ + X^- \]  
\tag{31}

The mass balance equation (27) is expressed as:

\[ C_M = [MX] + \text{[M}^+] \]  
\tag{29}

In which not ion pairing of the ions is presented due to a high polarity of the solvent, commonly water, with equilibrium constant defined by:

\[ K_s = \frac{a_{MX}a_{X^-}}{a_{MX^+}} \]  
\tag{32}

The application of this convention to the dissolution of salts has previously proved to be an efficient form to derive equations of states for model electrolyte solutions with multiple salts [27] and to predict the precipitation of salts from aqueous solutions using organic solvents [28]. This is possible as none of the scales in which the species concentration may be expressed is more fundamental than the others, and which scale is used is simply a matter of convenience.
\[ K_s = \frac{\gamma_{MXI}[M^+][X^-]}{x_{MXI}} \]  

(34)

Furthermore, as in such solutions \( \gamma_{MXI} \rightarrow 1, \gamma_{M^+} \rightarrow 1 \) and \( \gamma_{X^-} \rightarrow 1 \), Eq. (34) reduces to:

\[ K_s = \frac{[M^+][X^-]}{x_{MXI}} \]  

(35)

Substituting Eq. (28) in (35):

\[ K_s = \frac{[M^+][X^-]C_M}{(MXI)} \]  

(36)

which after rearrangement takes the form:

\[ \beta_s^* \frac{C_M}{K_s} = K_{f, \text{precipitate}} C_M = \frac{[MXI]}{[X^-][M^+]} \]  

(37)

The modified global formation constant \( \beta_s^* \) is basically the product of the formation constant of the precipitate, \( K_{f, \text{precipitate}} \), times the total concentration of the metal in solution. In the following sections, the utility of Eq. (37) will be further demonstrated.

**Ion Product**

Once again considering the same system, the fractions of the different metallic species exchanging the \( X^- \) anion are defined according to the previously shown theory (see acid base concepts) and using Eq. (37) as:

\[ x_{M^+} = \frac{[M^+]}{C_M} = \frac{[M^+]}{[M^+]+(MXI)} = \frac{1}{1+\beta_s^*[X^-]} = \frac{1}{1+K_s[K_s+[X^-]]} = \frac{K_s}{K_s+C_M[X^-]} \]  

(38)

\[ x_{MXI} = \frac{[MXI]}{C_M} = x_{M^+} \beta_s^*[X^-] = \frac{C_M[X^-]}{K_s+C_M[X^-]} = 1 - x_{M^+} \]  

(39)

From these equations and using Excel Figure 2a was created. It is clearly noted that when \( K_s > C_M[X^-] \), \( x_{M^+} > x_{MXI} \) and when \( K_s < C_M[X^-] \), \( x_{M^+} < x_{MXI} \); clearly at \( K_s = C_M[X^-] \), \( x_{M^+} = x_{MXI} \). Interestingly these observations based on the fraction of species concept just make it then equivalent the rules lying behind the comparison between the ion product concept and the \( K_s \) value as a mean to evaluate the degree of precipitation with those analyses done to evaluate the predominance of the different species in homogeneous ionic solutions, as this comparison determine the abundance of the soluble or insoluble metallic species, as shown below.

From Eq. (38) the generalization of the ion product concept to a continuous function which denotes the relationship between the fraction of soluble metal, \( x_{M^+} \), in a solution at \( C_M \) total metal concentration at a determined value of \([X^-]\) is given by:

\[ C_M[X^-] = \frac{K_s(1-x_{M^+})}{x_{M^+}} \]  

(40)

From this it is possible to evaluate that if \( x_{M^+} = 0.999 \) (99.9% predominance of \( M^+ \)):

\[ C_M[X^-] = \frac{K_s(1-0.999)}{0.999} \approx 0.001 K_s \]  

(41)

so that the ion product equals one thousandth of the \( K_s \) value, i.e., \( C_M[X^-] < K_s \) and the soluble species is more abundant than the precipitated one in agreement with the regular rules to evaluate precipitation reactions.

If \( x_{M^+} = 0.001 \) (0.1% predominance of \( M^+ \)):

\[ C_M[X^-] = \frac{K_s(1-0.001)}{0.001} \approx 1000 K_s \]  

(42)

so that the ion product equals thousand times the \( K_s \) value, i.e., \( C_M[X^-] > K_s \) and the precipitated species is more abundant than the soluble one in agreement with the regular rules to evaluate precipitation reactions.

Clearly at \( x_{M^+} = 0.5 \) this equation simplifies to \( C_M[X^-] = K_s \), the classical ion product, and both species have the same abundances in accordance with Figure 2b.

Certainly, it should possible to deduce approximate equations for the concentrations of species in logarithmic form without the need of computing the fraction of species in a similar form to that exemplified in acid/base reactions. Therefore, for the sake of symmetry in the representation, by defining:

\[ K_{d,1}^* = \frac{[X^-][M^+]}{(MXI)} \]  

(43)

and using the mass balance Eq. (29) when \( pX < pK_{d,1} \), \( \{MX\downarrow\} \gg \{M^+\} \) and \( \{MX\downarrow\} \approx C_M \); thus, two lineal forms, one for each species can certainly be deduced:

\[ log\{MX\downarrow\} = logC_M \]  

(44)

\[ log\{M^+\} = -pK_{d,1}^* + logC_M + pX \]  

(45)

Similarly, when \( pX > pK_{d,1} \), \( \{MX\downarrow\} \ll [M^+] \) and \([M^+] \approx C_M \) and

\[ log\{M^+\} = logC_M \]  

(46)

\[ log\{MX\downarrow\} = pK_{d,1}^* + logC_M - pX \]  

(47)

To perform a comparison between both procedures Eqs. (38) and (39) are transformed to their logarithms forms to get:

\[ log\{M^+\} = logC_M + logx_{M^+} \]  

(48)

\[ log\{MX\downarrow\} = logC_M + logx_{MXI} \]  

(49)

In Figure 2b it is seen that the horizontal line at \( logC_M = log\{MX\downarrow\} \) or \( log\{M^+\} \) is a graphic representation of the mass balance condition (Eq. (29)), and the equilibrium condition (Eq. (37)) is represented by the two straight lines given by Eqs. (47) and (49). In Figure 2b both procedures are compared as well. It is also worth to observe that strictly speaking the concept that precipitation “starts” when \( K_s = C_M[X^-] \) in this conceptualization is just a limiting condition generated
by the lineal approximation of the fraction diagram by
the lineal logarithmic equations, in the same way as
discussed in the acid/base case pointed out before, as
the condition at which the ion product equals the
solubility product constant determines in fact 50% of
precipitation (0.3 units below the mass balance
condition in a logarithmic representation). This result
will be further confirmed by numerical methods in its
corresponding section. The implications of such
statement will be analyzed further below as well.

It is also straightforward to write down a PZD from
Figure 2b considering that the system’s point,
$pX_{50\% \text{ abundance}}$, distinguishing the predominance zone
of the different species (analogous to the $pK_a$ value in
acid/base systems) is given by:

$$pX_{50\% \text{ abundance}} = \log \beta_i^* = pK_a + \log C_M = pK_a^*$$

This means that the $pK_a$ parameter must be
modified by a term accounting for the total
concentration of the analyte ($\log C_M$) to be useful as
coeexistence line value is this type of heterogeneous
systems, as it has been experimentally observed. The
combination of both terms defines a modified system
point ($pK_a^*$) from which the PZD can be draw as
shown in Figure 2c.

The behavior predicted by the model line
corresponding to the fraction of species of the
precipitate shown in Figure 2 can be explained
considering that in solutions of very low concentrations
of precipitating reagent ($pX > pK_{d,1}^*$) the number of
growth units per unit volume of solution is small and the
growth units are relatively distant from one another.
With the increase in concentration the unsaturated
solution gradually reaches supersaturation ($pX < pK_{d,1}^*$)
and spontaneous nucleation will happen when
the supersaturation reaches a certain value ($pX = pK_{d,1}^*$).
Between the unsaturated area and spontaneous
nucleation area a metastable zone exists, in which
spontaneous nucleation cannot happen without seed
crystals, unless concentration reaches the nucleation
zone. Then these nuclei can grow into crystals of
visible sizes in the supersaturated system, giving rise
to phase separation, and quantitative precipitation
initiates. The most interesting point of the fraction of
species treatment is the prediction of the presence of
precipitation units before phase separation, i.e., before
visual confirmation of precipitation (continuous curve in
the unsaturated region). The understanding of the
molecular mechanisms underlying phase separation
and the formation of the first solid particles in aqueous
solution during crystallization is rather limited. However,
stable solute species, often called pre-nucleation
clusters (PNCs), can exist in under-and supersaturated
solutions, and participate in the process of phase
separation. The role that PNCs have as solute
precursors in the emergence of a new phase has
recently been summarized, and the link between the
chemical speciation of homogeneous solutions and the
process of phase separation via pre-nucleation clusters
highlighted as well [29]. The stoichiometry of
constituents in the PNCs may resemble that of the bulk
phase with the addition of hydration water, as well as
hydroxide or hydronium ions. Recent experimental
and computational results suggest that Ca$^{2+}$ and CO$_3^{2-}$ ions
can associate into stable complexes prior to the
onset of liquid or solid CaCO$_3$ formation [30, 31]. Titration
experiments coupled to characterization techniques
have proved to be a form to study ion pairing and
clustering phenomena in the pre-nucleation regime [32].
So that, the presence of latent particles of precipitate in
the region in which $pX > pK_{d,1}^*$ assumed by the
heterogeneous speciation fraction is then compatible
with the presence of PNCs. However, further research
in this topic is needed before drawing additional
conclusions.

Figure 2: (a) Distribution diagram of a metal ion/precipitate
system with $pK_a = 10$ as a function of $pX$ at $C_M = 1mM$
computed from Eqs. (38) and (39) using Excel. (b)
Logarithmic diagram of the same system showing the
concentration of the species as a function of $pX$. The diagram
was constructed using Eqs. (44) to (47) and Eqs. (48) and
(49) for comparative purposes. (c) PDZ diagram constructed
from the above Figures showing the predominant species in
each $pX$ zone defined by the $pK_{d,1}^*$ value.

$$M_nX_m \downarrow \text{system}$$

The generalization of the above equations to a
precipitate with a stoichiometry ratio different to one
leads to:

![Image of Figure 2]
Precipitation Equilibrium
\[ M_n X_m \rightleftharpoons nM^{m+} + mX^{n-} \] (51)

Fraction of soluble metal
\[ x_M = \frac{K_s}{k_s + c_M^{x_m}} \] (52)

Ion Product
\[ c_M^{n}[X^{-}]^m = \frac{k_s(1-x_M)}{x_M^{n+}} \] (53)

System Point
\[ pX_{50\% \text{ abundance}} = \frac{pK_d \cdot n}{m} = \frac{1}{n} \log c_M \] (54)

Modified Stability Constant
\[ \beta_{n,m}^{*} = \frac{1}{n} \frac{c_M}{K_s} = \frac{\left(\frac{M_0 X_1}{M^{n+}}\right)^m}{x_M^{n+}} \] (55)

In this form, the \( pK_{d,n,m}/m \) parameter plays the same role in precipitation reactions than that play by \( pK_{d,n,m}/m \) in generalizing complexation reactions in homogeneous systems [3, 5, 6, 16].

Evidently, in a case of a homogeneous system with concentration \( C_x \) where \( MX \downarrow \) is continuously formed due to progressive additions of the precipitating reagent \( M^{n+} \), and \([M^{n+}]\) can be measured and/or controlled, the fraction of the different anion species exchanging the \( M^{n+} \) anion is defined in a similar way:

Fraction of soluble anion
\[ x_X^{-} = \frac{[X^{-}]}{c_X} = \frac{K_s}{K_s + c_X^{n}[M^{n+}]^m} \] (56)

Ion Product
\[ c_X^{n}[M^{n+}]^m = \frac{k_s(1-x_X^{-})}{x_X^{-}} \] (57)

System Point
\[ pM_{50\% \text{ abundance}} = \frac{pK_d \cdot n}{m} = \frac{1}{n} \log c_X \] (58)

In this form Eqs. (54) and (58) perfectly agree with previous efforts to correlate precipitations reactions with other ionic equilibria through establishment of PZD diagrams [18].

3. APPLICABILITY OF THE NEW DESCRIPTION AND COMPATIBILITY WITH OTHER APPROACHES THROUGH THE ANALYSIS OF COPPER (II) HYDROLYSIS

The reliability and utility of the heterogeneous fraction of species concept in the description of precipitation reactions were established by comparing its results with two different established numerical and graphical approaches using the hydrolysis of copper (II) at three different total concentrations (1µM, 10 µM, and 1mM) as illustrative example of application, as described below.

Equilibrium Computation Using Numerical Methods

First, the MEDUSA (Make equilibrium diagrams using sophisticated algorithms) software [33] was used to draw fraction diagrams for the system (Figures 3a-c). The program is based on the SOLGASWATER [34], and HALTAFALL [35] algorithms which allow the computation of the chemical equilibrium composition of a system by two procedures: i) minimization of the free energy of the system, and ii) solving non-linear equations associated with the law of mass action using the master variable approach, respectively. As observed each of the soluble \( Cu^{2+} \), \( Cu(OH)^{2+} \), \( Cu(OH)_{2}^{+} \), \( Cu(OH)_{3}^{2-} \), \( Cu(OH)_{4}^{2-} \), and the \( Cu(OH)_{2} \downarrow \) solid species has characteristic predominance pH regions determined by the equilibrium constants of the copper (II)-hydroxide complexes (\( \beta_{l} \)), the solubility product constant value (\( K_s \)) and the total concentration of the metal ion (\( c_{Cu} \)). Clearly \( Cu(OH)^{2+} \) and \( Cu(OH)_{3}^{2-} \) species with low predominance, i.e., low \( x_{Cu(OH)^{2+}} \) values, in the concentration range studied, reason why the \( Cu^{2+} \), \( Cu(OH)_{2} \downarrow \), and \( Cu(OH)_{3}^{2-} \) species completely determines each PZD that can be drawn for Figures 3a-c. As expected, the pH value at which the solid species starts to predominate is a function of \( c_{Cu} \). The logarithm diagram of all the species was additionally numerically computed and drawn at \( c_{Cu} = 1 \mu M \) with the same software. From Figure 3d, it is clear that the polynuclear \( Cu_{2}(OH)_{2}^{3+} \) species plays a minor role in the equilibrium composition of the system at this copper concentration.

In the absence of the polynuclear complex, the fractions of species for all participating species are expressed as previously discussed (see acid base section) as:

\[ x_{Cu^{2+}} = \frac{[Cu^{2+}]}{c_{Cu}} = \frac{[Cu^{2+}]}{\sum_{l=1}^{n}[Cu(OH)^{2+}]_{l} + [Cu(OH)_{2}^{+}]_{l}} \] (59)

\[ x_{Cu(OH)^{2+}} = \frac{[Cu(OH)^{2+}]}{c_{Cu}} = \frac{[Cu(OH)^{2+}]}{1 + \sum_{l=1}^{n}[OH^{-}]_{l} + \beta_{l}[OH^{-}]^{2}} \] (60)

\[ x_{Cu(OH)_{2}^{+}} = \frac{[Cu(OH)_{2}^{+}]}{c_{Cu}} = x_{Cu^{2+}} + \beta_{l}[OH^{-}] \] (61)

with

\[ \beta_{l} = \frac{c_{Cu}}{K_s} \cdot \frac{[Cu(OH)_{2}^{+}]}{[OH^{-}]^{2}[Cu^{2+}]} \] (62)

As Eqs. (59) to (61) depend only on pH they are easily draw with Excel considering the same equilibrium constants values used in MEDUSA evaluations (Figures 4a-c, \( Cu^{2+}/OH^{-}: log \beta_{2} = 6.04 \), \( log \beta_{3} = 11.76 \), \( log \beta_{4} = 15.3 \), \( log \beta_{4} = 16.4 \), \( pK_s = 19.84 \)). The comparison of these diagrams with those obtained with the numerical software reveals the
Figure 4d shows the comparison of the result obtained with this treatment with that obtained using MEDUSA ($\log \beta_{2.2} = 17.65$). As observed, comparable results are obtained from the fraction of species concept and the solution of the concentrations of the system by numerical methods.

Equilibrium Calculations Using Graphical Methods

Another way to get an idea of the distribution of the different species in a complex system is to use logarithmic relative diagrams. In this representation one species is selected as reference and the logarithmic ratios of the concentration between a specific species and the reference one is obtained using the equilibrium constants of the system. The relative diagram is easy to construct even in cases of several overlapping equilibria and has also found use in representing redox equilibria [4, 36]. In Figure 5a and using Excel such diagram is plotted for copper (II) hydrolysis at $C_{Cu} = 0.1 \text{mM}$ taking as reference $[Cu^{2+}]$. The equations for the relative concentrations considering the same equilibrium constants used with MEDUSA evaluations are:

$$\log \frac{[Cu^{2+}]}{[Cu^{2+}]} = 0$$

$$\log \frac{[Cu(OH)^+]^{2}}{[Cu^{2+}]} = \log \beta_1 + \log K_w + pH = -7.96 + pH$$

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where it was assumed that $K_w = 10^{-14}$. As observed, the different predominance zones previously observed in Figure 3a are clearly distinguished. However, this time the predominance of a species is determined by the uppermost straight line in each region. It is important to mention that Eq. (72) has a different meaning than the previous ones (67-71) as it serves as an auxiliary line from which precipitation can be analyzed. For the studied system, the precipitation condition in this type of representation is given by the following condition [36]:

$$\log \frac{[\text{Cu(OH)}]}{[\text{Cu}^{2+}]} = \log g_2 + 2\log K_w + 2pH = -16.24 + 2pH \quad (69)$$

$$\log \frac{[\text{Cu(OH)}]}{[\text{Cu}^{2+}]} = \log g_3 + 3\log K_w + 3pH = -26.7 + 3pH \quad (70)$$

$$\log \frac{[\text{Cu(OH)}_2]}{[\text{Cu}^{2+}]} = \log g_4 + 4\log K_w + 4pH = -39.6 + 4pH \quad (71)$$

$$\log \frac{[\text{Cu(OH)}_2]}{[\text{Cu}^{2+}]} = -\log K_z + 2\log K_w + 2pH = -8.16 + 2pH \quad (72)$$

which according to the diagram is accomplished at pH = 7.1, in agreement with the previous numerical results (Figure 3a) and in agreement with the evaluation using Eq. (54).

Although the diagram shown in Figure 5a is very useful, it is not very easy from it to determine the predominance zone of Cu(OH)$_2$. The logarithmic relative diagram representation can be further improved including Eq. (62) in the graphical treatment in the same form as done with the soluble species to obtain a new relationship that replaces Eq. (72):

$$\log \frac{[\text{Cu(OH)}_2]}{[\text{Cu}^{2+}]} = \log g_2 + 2\log K_w + 2pH = -14.2 + 2pH \quad (74)$$

This equation represents a true relative abundance line of the precipitate, as Eqs. (67) to (71) do. In Figure 5b, the modified logarithmic relative diagram including Eqs. (67) to (71) and (74) is presented. As shown, this diagram allows a straightforward visualization of the predominance zone of the precipitate making easier to draw the PZD shown below (Figure 5c). This PDZ is in perfect agreement with results shown in Figures 3a and 3d.
4. INCORPORATION OF THE HETEROGENEOUS FRACTION OF SPECIES CONCEPT IN TITRATION CURVES AND SIDE-REACTION (SPECIATION) COEFFICIENTS

Generalized Titration Curves

Following the procedure reported by de Levie [37] to compute acid/base, complexometric, and redox titration curves using explicit equations in terms of concentration, it is possible to generate that representation corresponding to the precipitation titration of Cu$^{2+}$ (dissolved initially as an strong electrolyte with initial volume $V_a$ at $C_{Cu}$ concentration), considering the presence of its soluble complexes $Cu(OH)^{+}$, $Cu(OH)_2^-$, $Cu(OH)_3^{2-}$ besides the $Cu(OH)_2$ solid species, through additions of the reagent $OH^−$ (added as the strong electrolyte with $v_{ad}$ volume at $C_{OH}^−$ concentration) as further described.

Taking into account $Cu^{2+}$ and $H_2O$ as references, the proton condition of the system [4] is expressed by:

$$[H^+] - [OH^-] - \sum_{i=1}^{n} [Cu(OH)^{+}] - 2[Cu(OH)_2] = \frac{C_{OH}^- v_{ad}}{C_{Cu} V_0}$$ (75)

which can be expressed in terms of $\beta_{i}$ as:

$$[H^+] - [OH^-] - [Cu^{2+}] \sum_{i=1}^{n} \beta_{i} [OH^-]^i + 2\beta_{2} [OH^-]^2 = \frac{C_{OH}^- v_{ad}}{C_{Cu} V_0}$$ (76)

Incorporating the heterogeneous fraction of species concept, Eq. (63), the above equation transforms to:

$$[H^+] - [OH^-] - \left(\frac{C_{Cu} V_0}{V_0 + v_{ad}}\right) Z = -\frac{C_{OH}^- v_{ad}}{C_{Cu} V_0}$$ (77)

previous identification of the $Z$ function [4], the average number of protons bound per $Cu^{2+}$ species:

$$Z = \sum_{i=1}^{n} \left(\frac{[OH^-]^i}{\beta_{i} [OH^-]^i} \right)$$ (78)

Defining the fraction of titration, $F$, as:

$$F = \frac{C_{OH}^- v_{ad}}{C_{Cu} V_0}$$ (79)

once the autoprotolysis of water was included Eq. (77) is finally expressed as:

$$F = \frac{Z [OH^-] [Cu^{2+}]}{1 + [Cu^{2+}] [OH^-]}$$ (80)

This equation is important as it points out the degree of titration as a function of the evolution of the homogeneous fraction of species of $Cu^{2+}$, as expected, in symmetry with the homogeneous fractions of species in acid/base, complexometric, and redox titrations [10]. As Eq. (80) express $F = f([H^{+}])$, it is possible to evaluate $F$ for given values of $pH$ using a spreadsheet. In Figure 6 the titrations of several initial concentrations of $Cu(NO_3)_2$ with 0.01 mM NaOH are shown. Clearly, Eq. 80 perfectly describes the expected behavior.

Homogeneous Side-Reaction Coefficients

Introduced by Gerold Schwarzenbach [19] and Anders Ringbom [20], side-reaction or speciation coefficients allow a simple form to account for the effect

\[\text{Certainly, the deduction of continuous equations to represent titration curves for precipitation reactions is not new [13, 38], but previous approaches have not expressed the fraction of titration considering the presence of concomitant soluble species with a common ion, as done in the present method.}\]
of simultaneous collateral reactions in a specific ionic equilibrium that is under study (the main reaction).

\[ \text{Cu}^{2+} + L^{2-} \leftrightarrow \text{Cu}L^{2-z}^{-} \]  
(81)

\[ \beta' = \frac{[\text{CuL}^{2-z}^{-}]}{[\text{Cu}^{2+}][L^{2-}]} \]  
(82)

where \( \text{Cu}^{2+} \) stands for the metal in all dissolved forms except \( \text{CuL}^{2-z}^{-} \), \( L^{2-} \) for the ligand in all dissolved forms except \( \text{CuL}^{2-z}^{-} \), and \( \text{CuL}^{2-z}^{-} \) for all forms of the reaction product.

According to the previous sections and using the data in Table 1 at \( C_{\text{Cu}^{2+}} = 0.1 \text{mM} \), conditional mass balance equations for all participating species in the main reaction are expressed as:

\[ [\text{Cu}^{2+}] = [\text{Cu}^{2+}] + \sum_{i=1}^{4} [\text{Cu}(OH)^{z-}]_{i} = [\text{Cu}^{2+}] (1 + \sum_{i=1}^{4} \beta_{i}[\text{OH}^{-}]) \]  
(83)

\[ [L^{2-}] = [L^{2-}] + \sum_{j=1}^{4} [H_{j}L^{j-z}^{-}] = [L^{2-}] (1 + \sum_{j=1}^{4} \beta_{j}[H^{+}]) \]  
(84)

\[ [\text{CuL}^{2-z}^{-}] = [\text{CuL}^{2-z}^{-}] + [\text{CuLH}^{3-z}] = [\text{CuL}^{2-z}^{-}] (1 + \beta_{\text{CuL}^{2-z}^{-}[H^{+}]) \]  
(85)

where the side reaction coefficients, \( \alpha_{i} \), accounting for quantitative representations of all the competing side-reactions which tend to change the extent to which the main coordination reaction proceeds, are defined as:

\[ \alpha_{\text{Cu}^{2+}[\text{OH}^{-}]} = \frac{[\text{Cu}^{2+}]}{[\text{Cu}^{2+}]} = 1 + \sum_{i=1}^{4} \beta_{i}[\text{OH}^{-}] \]  
(86)

\[ \alpha_{L^{2-}[H^{+}]} = \frac{[L^{2-}]}{[L^{2-}]} = 1 + \sum_{j=1}^{4} \beta_{j}[H^{+}] \]  
(87)

\[ \alpha_{\text{CuL}^{2-z}^{-}[H^{+}]} = \frac{[\text{CuL}^{2-z}^{-}]}{[\text{CuL}^{2-z}^{-}]} = 1 + \beta_{H}^{+}[\text{CuL}^{2-z}^{-}[H^{+}] \]  
(88)

The relationship between both constants is then given by:

\[ \beta' = \beta - \frac{\alpha_{\text{CuL}^{2-z}^{-}[H^{+}]} \alpha_{\text{Cu}^{2+}[\text{OH}^{-}],L^{2-}[H^{+}]} \text{Cu}^{2+} \text{Cu}L^{2-z}^{-} \text{CuLH}^{3-z}] \]  
(89)

From this equation, it is clear that \( \beta' \) has different values according to the pH of the solution, i.e., at pH = 7.0 \( \beta' = 10.5^{26} \), where the predominant species of copper (II) in the homogeneous system is \( \text{Cu}^{2+} \), while at pH= 9.5 the predominance of the \( \text{Cu(OH)}_{2} \) soluble species reduces \( \beta' \) to 10.44 (80). However, these usual determinations of the \( \alpha_{i} \) coefficients have been independent on considering precipitation reactions, in spite that insoluble hydroxide complexes may be formed depending on copper concentration (Figures 3). If precipitation does occur, the solubility product constant fixes the dissolved free metal ion concentration, and the concentrations of all other dissolved species; consequently, the side-reactions coefficients should be affected in a form that cannot be easily accounted from the above equations.

**Table 1: Reported Copper (II) / H⁺ / Pectin (L⁻) Global Equilibrium Constants at 0.1 M of Ionic Strength**

<table>
<thead>
<tr>
<th>Equilibrium</th>
<th>( \log \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L^{2-} + H^{+} \leftrightarrow HL^{3-z}^{-} )</td>
<td>3.77</td>
</tr>
<tr>
<td>( HL^{3-z}^{-} + H^{+} \leftrightarrow H_{2}L^{2-z}^{-} )</td>
<td>6.94</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + L^{2-} \leftrightarrow \text{Cu}L^{2-z}^{-} )</td>
<td>5.31</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + L^{2-} + H^{+} \leftrightarrow \text{CuLH}^{3-z} )</td>
<td>8.66</td>
</tr>
</tbody>
</table>

As an example of application, it is known that pectin (\( L^{2-} \), where \( z = \text{effective charge of the polyelectrolyte} \) is a polysaccharide that is largely present in the cell wall of plants, and in the flesh and peels of many fruits. It is used as gelling agents for food and as stabilizers for pulp drinks, in the production of biodegradable films for foods and in the pharmaceutical industry, as a carrier for drugs. Due to the presence of multiple carboxylate-binding sites in its structure, pectin can act as a sequestering agent for metal ions. For such reason, its use in different technical applications such as water and wastewater treatment, heavy metal removal in contaminated sites, metal recovery, etc. has been studied. At 0.1 M of ionic strength the following equilibrium constants are reported [39]:

**Figure 6:** Titration curves of \( \text{Cu(NO}_{3} \text{)}_{2} \) with 0.01 mM NaOH at different initial copper (II) concentrations. The presence of the soluble complexes (\( \text{Cu(OH)}^{+} \), \( \text{Cu(OH)}_{2} \), \( \text{Cu(OH)}^{2+} \)) as well as the \( \text{Cu(OH)}_{2} \) solid species was considered in the simulation.
Heterogeneous Side-Reaction Coefficients

Up to now, no information concerning the inclusion of precipitation reactions in side-reactions coefficients can be found in the literature in spite that commonly different insoluble species may be present in the system, e.g., hydroxide precipitates. This is a consequence of the extend use of the ion product or the use of logarithm diagrams to explain precipitation reactions, as these representations do not allow a simple incorporation of precipitation in the $\alpha_i$ mathematical structure. However, the inclusion of the fraction of species framework allows a straightforward generalization of side-reaction coefficients to heterogeneous systems due to the compatibility in structure that the heterogeneous fraction has with the homogeneous ones (Figures 1 and 2). In such form, Eq. (83) is easily transformed to:

$$[\text{Cu}^{2+}] = [\text{Cu}^{2+}_1] + \sum_{i=1}^{4}[\text{Cu}(\text{OH})_2]^{i-1} + [\text{Cu}(\text{OH})_2^{-1}] + [\text{Cu}(\text{OH})_2^{-1}]^{i+1} = [\text{Cu}^{2+}_1](1 + \sum_{i=1}^{4}\beta_i[\text{OH}^-]^i + \beta_2^2[\text{OH}^-]^2) \quad (90)$$

with

$$\alpha_{\text{Cu}^{2+}(\text{OH}^-)} = \frac{[\text{Cu}^{2+}_1]}{[\text{Cu}^{2+}]} = 1 + \sum_{i=1}^{4}\beta_i[\text{OH}^-]^i + \beta_2^2[\text{OH}^-]^2 \quad (91)$$

The last term in Eq. (91) has its usual meaning, i.e., relative abundance of the $\text{Cu}(\text{OH})_2^{-1}$ species, which depends on $C_{\text{Cu}^{2+}}$ by $\beta_2^2$, as expected.

5. CONCLUSIONS

The generalization of the fraction of species concept to precipitation reactions allows an easy form to fully integrate the ion product concept in a general ionic framework of homogeneous solutions, to obtain PDZ diagrams for soluble and insoluble species, to enrich the use logarithmic relative diagrams, to generate titration curves, and to generalize side-reaction coefficients to heterogeneous systems. The inclusion of precipitation reactions in the general ionic equilibrium framework of homogeneous solutions (acid/base, redox, and complex systems) is performed in a straightforward form using a modified equilibrium constant value, which is the constant corrected by the total concentration of the analyte, with the advantage that the structure of the fundamental equations and representations of the homogeneous solution framework is positively conserved. It was demonstrated that this modified and thermodynamically supported constant together with the implications of the approach are compatible with pre-nucleation clusters (PNCs) theory and well-established numerical and graphical methods of evaluation of solution equilibria. The new representation was successfully applied in the study of the hydrolysis of copper (II) in the absence and the presence of complexing ligands considering the precipitation of its hydroxide species using easy-to-compute algorithms of calculation.

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