ON HOW TO PREDICT THE APPEARANCE OF A PRECIPITATE IN REACTIONS OF THE TYPE A + B ⟶ AB↓

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A mathematical model is developed based on the equilibrium A + B ⇌ AB↓ ,Ksp, which originates when aqueous solutions of A and B are mixed. The model not only allows one to predict the appearance of a precipitate in a given experimental situation but it also permits one to influence the parameters of the reaction, in order to obtain, or prevent, the formation of a precipitate.

INTRODUCTION

The traditional textbooks of Analytical Chemistry, while presenting the analysis of aqueous solutions in which an equilibrium of the kind

$$A + B \rightleftharpoons AB\downarrow \text{ , Ksp,} \qquad (1)$$

may lead to precipitation, usually do so in a manner which does not allow visualization of the chemical fenomenum, since they only treat isolated cases, considering only if there is precipitation or there is not.

In this paper we intend to show that the approach of the problem can be done in a generic manner.

DEVELOPMENT

Let us suppose an aqueous medium, in which the ionic chemical species A and B, different from H^+ and OH^-, are capable of reacting with each other as shown in the equilibrium represented by equation 1. Let us suppose it is known the value of the equilibrium constant for the conditions in which the reaction is to take place; i.e., if A and/or B participate simultaneously in another reaction besides the one described by equation 1, the equilibrium constant to be used is the conditional Ksp. Otherwise, the formal Ksp should be the one to be used.

Let us suppose now that one has solutions of A and B, having molar analytical concentrations CA and CB, respectively. Suppose, finally, that to a given volume VA of the species A are added successive known volumes VB of B.

The equation which allows one to calculate values of VB which will bring about precipitation can be deduced according to the following:

By definition, for any given value of VB $\geqslant$ 0

$$C_1 = CAVA / (VA + VB)$$

$$C_2 = CBVB / (VA + VB)$$

$$J = C_1 C_2$$

one can observe:

a. if the value of VB is very small, C_1 and C_2 will apprach CA and zero, respectively, and J will be smaller than Ksp. Consequently there will be no precipitation under these conditions;

b. if the value of VB is very large, C_2 and C_1 will approach CB and zero, respectively; again J will be smaller than Ksp, and, again, there will be no precipitation under these conditions;

c. there is an interval of values of VB ($0 < VB < \infty$) for which precipitation will occur, with consequent formation of AB↓. For a saturated solution, without any precipitate, one must have

$$J = Ksp,$$

therefore the values of VB that fulfill this equality are the ones that define the limits of this interval. Therefore, considering the definitions of C_1, C_2 and J, one has

$$CAVACBVB / (VA + VB)^2 = Ksp$$

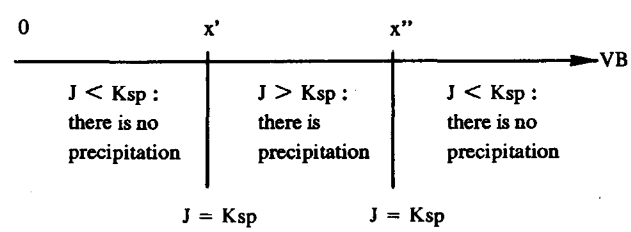
which leads to

$$Ksp\,(VB)^2 + [\ VA(2\ Ksp - CACB)\ ]\ VB + Ksp\,(VA)^2 = 0 \qquad (2)$$

This is a polynomial expression of the type:

$$ax^2 + bx + c = 0 \qquad (3)$$

and the roots, x' and x", of this expression correspond to the values of VB in which the solution will be exactly saturated. In a schematic manner, we have:



This scheme shows in a logical manner the behaviour of the system.

As an example let us consider: CA = 10^{-4}M VA = 100 ml, CB = 10^{-4} M and Ksp = 10^{-9}. Using equation 2, we obtain:

x' = 12.7 ml and x" = 787.3 ml".

ANALYSIS OF THE MATHEMATICAL MODEL

Given the nature of the problem, a mathematical analysis of the proposed model will lead, among others, to the following considerations:

1. Equation 3, when applied to the proposed problem, since $Ksp > 0$, $VA > 0$ and $VB > 0$, will give $a > 0$ and $c > 0$.

Under this circunstance, the relationship between the numerical values of b and the roots will be:

1.a If $b \geqslant 0$: x' and x" will have negative or complex values.

1.b If $b < 0$: there will be 3 possibilities:

- when $(b^2 - 4ac) < 0$: x' and x" will be complex;

- when $(b^2 - 4ac) = 0$: x' will be equal to x" and will have real positive values;

- when $(b^2 - 4ac) > 0$: x' will be different from x" and both will have real positive values.

The results show that there are only two possibilities (the last two ones) to solve the problem under consideration.

2. Since x' and x" must have real, positive values, equation 3 can only be used when:

$$b^2 - 4ac \geqslant 0$$

or, considering equation 2, when:

$$[VA\,(2Ksp - CACB)]^2 - 4Ksp(VA)^2 \geqslant 0$$

Therefore when:

$$CACB \geqslant 4\,Ksp \qquad (4)$$

As a result of obeying both the nature of the problem and equation 4, by using equation 2, one will obtain always roots which will have real, positive values, in accordance with the numerical example given.

3. If a given situation leads to the limit imposed by equation 4, i.e., $CACB = 4Ksp$, use of equation 2 will give:

$$x' = x'' = VA$$

indicating that with the system under consideration, one can obtain a satured solution (when $VA = VB$) however, without ever producing a precipitate. This hypothesis, when applied to the case in which one has: $CA = 4.10^{-5}$ M, $VA = 100$ ml, $CB = 10^{-5}$ M and $Ksp = 10^{-10}$, leads to $VB = x' = x'' = 100$ ml.

4. If one intends to have a situation in wich $CACB < 4\,Ksp$, the use of equation 2 will lead to complex values for both the roots, as expected. In this case, one can say that by mixing solutions of A and B, under no circunstance precipitation or, even, a satured solution will be attained.

CONCLUSIONS

The rationale so far exposed shows that for equilibria which can be described by equation 1, one can, among other things:

I. predict formation of a precipitate, given fixed experimental conditions;

II. to fix experimental conditions, so as to obtain, or prevent, precipitations, as desired;

III. to show that the analysis of the mathematical model which describes the chemical fenomenum if of fundamental importance, since it may constitute, as in this case, an excellent means to visualize this chemical fenomenum.

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