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ON THE EXISTENCE AND UNIQUENESS OF A CHEMICAL ROOT IN IONIC EQUILIBRIUM PROBLEMS

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ABSTRACT

Ionic equilibrium problems deal with algebraic equations of high degree. Textbooks discuss approximate methods for finding the numerical value of the chemically important root but no one proves the existence and uniqueness of that root.

It is our purpose here to show that two important theorems of the theory of algebraic equations can be used to demonstrate the existence and uniqueness of a "chemical root" in problems of ionic equilibrium.

RESUMEN

La solución exacta de problemas de equilibrio iónico implica la resolución de ecuaciones algebraicas de alto grado. Los libros de texto discuten métodos aproximados para encontrar la raíz con sentido químico pero ninguno demuestra la existencia y unicidad de esa raíz.

Es nuestro propósito en este trabajo demostrar la existencia y unicidad de la "raíz química" por medio de dos importantes teoremas de la teoría de ecuaciones algebraicas.

The exact solving of ionic equilibrium problems implies the calculation of roots of high degree algebraic equations. The unknowns being the concentrations of ions in equilibrium, for example, $[H_3O+]$, $[OH^-]$, $[Ag^+]$, etc. Even the exact treatment of a simple equilibrium such as that of a weak monoprotic acid in water leads to a cubic equation[1]. More complicated equilibria as dissociation of complex ions in water can lead to equations of degree eight and higher. Textbooks discuss these problems using approximations for finding the "chemical interesting solution" but no one establishes a criterium for the existence and uniqueness of a chemical important root in the range of allowed concentrations. It is simply assumed that only one root of chemical interest exists in the range of concentrations allowed. This assumption is a consequence of the law of mass conservation and of the fact that in our physical world only positive concentrations exist. Solving high degree algebraic equations means iterative methods and in our days using a computer[2]. It seems to be imperative for this purpose to assure that only one root, chemically possible, exists.

In a recent approach, Ludwig[3] tries to answer the student's question: How do you know that the other root(s) of the equilibrium equation are

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(1) *BUTLER, JAMES, "Ionic Equilibrium a Mathematical Approach", Addison-Wesley, Massachusetts, 1964.*

(2) *We have dealt with this in a seminar sponsored by Unesco: Elaboración de Módulos de Interrelación entre Matemáticas y Química. Caracas 1984. Results will be published by Unesco-Orealc.*

(3) *LUDWIG, D.G., J. Chem. Educ. 60, 547. (1983).*

physically impossible? In that approach is is assumed that only one root exists in the range of concentrations considered and then proceeds to show, using what is known in the theory of algebraic equations as Viete's relations[4], that the other root(s) are chemically impossible, i.e. they give negative concentrations or concentrations out of the limits of possible ones. However, the application of Viete's relations becomes more difficult when the degree of the equation is greater than two.

Here we present a method to demonstrate the existence and uniqueness of a root, "the chemical root", in ionic equilibrium problems in the interval allowed by the chemical restrictions. The method is based on two theorems of the theory of algebraic equations. Here we will restrict the method to the study of the existence and uniqueness of a chemical root in three kinds of ionic equilibrium: solubility of salts, complex ions and dissociation of a weak monoprotic acid; however, the theorems can be applied to other kinds of ionic equilibrium.

The first theorem (labeled from here on as theorem 1) says: if a real polynomial f(x), for $a \leq x \leq b$ takes values f(a) and f(b) of opposite signs, then there is at least one root of the equation f(x)=0 in the interval (a,b)[4]. This theorem will be used to show the existence of a chemical root in a given interval of concentrations.

Before stating the second theorem let us introduce first two definitions. Given a sequence of numbers a_0, a_1, $a_2,\ldots,a_n$, $a_i \neq 0$, if two consecutive numbers a_{i-1} and a_i have the same sign we say that they

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(4) USPENSKY, J.V. *Theory of Equations*, Mc. Graw-Hill, New York, 1948.

present a permanence of signs, if they have different signs we say that they present a variation of signs. Now we can state the following rule known as Descartes' Rule of Signs (and from here on referred to as theorem II): given the equation:

$$f(x) = a_n x^n + a_{n-1} + \ldots + a_0 = 0 \tag{1}$$

with real coefficients a_i, the number of positive real roots is equal to the number of variations of signs in the sequence of its coefficients (coefficients equal to zero do not count) or is less than this in an even number[4]. This theorem will allow us to prove the uniqueness of a chemical root in problems of ionic equilibrium. In what follows we will apply these two theorems to the three kinds of ionic equilibrium mentioned above.

SOLUBILITY EQUILIBRIUM

To illustrate the application of the theorem to this case we will consider the aqueous solution of a slightly soluble salt to which a substance has been added that has a common ion with the solute (common ion effect).

Consider the equilibrium of the slightly soluble salt $A_a B_b$ in water

$$A_b \; B_{b(s)} \rightleftharpoons aA^{+b}_{(aq)} + bB^{-a}_{(aq)} \tag{2}$$

The solubility ion product constant K_{sp} is given by

$$K_{sp} = [A^{+b}]^{\,a} \; [B^{-a}]^{\,b}. \tag{3}$$

Let A_0 be the concentration of the substance added and s the solubility of A_aB_b. Then, $[A^{+b}] = (A_0 + as)$; $[B^{-a}] = bs$ and equation (3) becomes:

$$K_{sp} = (A_0 + as)^a \; (bs)^b$$

$$= b^b \; A_0^a s^b \; b + \ldots + b^b \; a^a \; s^{a+b} \tag{4}$$

or

$$f(s) = b^b \; a^a \; s^{a+b} + \ldots + b^b \; A_0 \; a_s b - K_{sp} = 0 \tag{4'}$$

where all coefficients which do not appear are also positive quantities. Thus, there will be only one sign variation and consequently only one positive root. Finally, we will prove that this positive root lies in the range $0<s<s_{max}$, where s_{max} is equal to $(K_{sp}/a^a b^b)\,(a+b)^{-1}$, for $A_0 = 0$. The values of f(s) at 0 and s_{max} are

$$f(0) = -K_{sp}<0$$

$$f(s_{max}) = b^b \; a^a (s_{max})^{a+b} + \ldots + b^b \; A_0^a (s_{max})^b - K_{sp}. \tag{5}$$

Since $b^b \; a^a \; (s_{max})^{a+b} = K_{sp}$, then $f(s_{max}) > 0$ because all terms left are positive quantities. Then by Theorem I we conclude that at least one root exists in the interval $0<s<s_{max}$ and, as has been shown previously

by Theorem II, that root is unique.

EQUILIBRIUM OF COMPLEX IONS

Here we will consider only those complexes formed by one central ion and one type of ligand. Let us consider the dissociation of the complex AB_b where A is the central ion and B the ligand; the equilibrium equation is

$$AB_b \rightleftharpoons A^{+b} + bB^{-1} \tag{6}$$

The unstability constant of the complex K_i, will be given by

$$K_i = \frac{[A^{+b}]\ [B^{-1}]^b}{[AB_b]} \tag{7}$$

If x is the number of moles per liter of AB_b dissociating, then $bx = [B^{-1}]$ and $C-x = [AB_b]$, where C is the initial concentration of the complex. From equation (6) we find

$$K_i = \frac{x(bx)^b}{C-x} \tag{8}$$

or

$$f(x) = b^b\ x^{b+1} + K_i x - CK_i = 0. \tag{8'}$$

The number of variations of signs of this equation is one, therefore the equation will have only one positive root. To show the existence of that root in the range of concentrations $[0,C]$ we will calculate the function f(x) at the end points of the interval. From equation (8') we find

$$f(0) = - CK_i < 0$$

$$f(C) = b^b\, C^{b+1} > 0 \qquad (9)$$

Then, from Theorem I we conclude that at least one root exists in that interval. As shown before by Theorem II, that root is unique.

DISSOCIATION OF A WEAK MONOPROTIC ACID

The dissociation of a weak monoprotic acid in water leads to the following simultaneous equilibrium equations:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \; ; \; K_a = \frac{[H_3O^+]\;[A^-]}{[HA]}$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- ; \; K_w = [H_3O^+]\;[OH^-] \qquad (10)$$

The resultant algebraic equation whose solution gives the equilibrium concentration of H_3O^+ is the following:

$$f(x) = x^3 + K_a\, x^2 - (K_w + K_a C)\, x - K_a\, K_w = 0, \; x = [H_3O^+] \qquad (11)$$

where C is the initial concentration of HA, K_a the dissociation constant of HA, K_w the ion product constant of water. The interval of concentrations in which the values of x lie is $[K_w^{1/2}, C+K_w^{1/2}]$. The left hand value of the interval corresponds to the concentration of H_3O^+ when no dissociation of HA occurs; the right hand one corresponds to a complete dissociation of HA (strong acids)[5].

Because K_a, K_w and C are all positive quantities, the number of variations of signs of equation (11) is one. Thus, according to Theorem II, equation (11) has only one positive root. To show the existence of this root in the interval of concentrations given above, it will be necessary to determine the signs of $f(K_w^{1/2})$ and $f(C+K_w^{1/2})$. From equation (11) we find

$$f(K_w^{1/2}) = -K_a K_w C < 0$$

$$F(C+K_w^{1/2}) = C^3 + CK_w (3C + 2K_w + K_a) > 0 \tag{12}$$

so the function f(x) has different signs at the end points of the interval and according to Theorem I there will exist at least one root in that interval. The uniqueness of this root has been shown in Theorem I. More complicated acid-base equilibria like the dissociation of H_nA $(n=2, 3,\ldots)$ can be analyzed in the same manner.

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(5) *Strictly, the right side of the interval must be smaller than $C + K_w 1/2$ because by the Le Chatelier Principle, adding H_3O^+ ions to pure water diminishes dissociation. However, making this amendment will not have any influence on the conclusions.*

SUMMARY

We have shown that two theorems of the theory of algebraic equations can be used to prove the existence and uniqueness of a chemical root in ionic equilibrium problems. The methodology here presented can also be used to show the existence and uniqueness of a chemical root for problems in which several equilibria coexist. We have chosen general cases where the two theorems can be applied to give unambiguous answers. However, the method will not be enough to prove the existence and uniqueness of a chemical root in all chemical equilibrium cases. In those cases in which this method cannot give an unambiguous answer it will be necessary to consider each particular problem and apply a more powerful but much less easy to apply theorem like Sturm's which always gives the exact number of roots in a given interval[3].

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APPENDIX

Chemical equilibrium is a function of reactants' and products' concentrations. For a chemical reaction such as

$$aA + bB \rightleftharpoons cC + dD,$$

this function may be written, at constant temperature as:

$$K = \frac{[C]^c \; [D]^d}{[A]^a \; [B]^b}$$

where a, b, c, d are the coefficients of the chemical equation. These numbers are real, strictly positive, usually integers. The symbol $[A]$, for example, stands for the concentration, in moles per liter, of the substance A. In all cases $[A] > 0$ where A stands for any substance.