THE CALCULATION OF THE CHEMICAL SPECIES CONCENTRATIONS FROM THE ELECTROLYTES SOLUTIONS

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abstract: In this paper the study upon simultaneous chemical equilibria is continued. Its purpose is to calculate the chemical species concentrations from the solutions of some electrolytes. Its purpose is to calculate the chemical species concentrations in the solutions of some electrolytes.

Introduction

In this paper the study upon simultaneous chemical equilibria is continued.

It is known that by dissolving an electrolyte (acid, base, salts) in water it is formed a solution that contains the ions and neutral molecules resulted after the reactions which take place in the solution [1]. There is a large number of equilibrium reactions which can be written between the existent chemical species.

Research made on the electrolyte solutions has indicated complex mechanisms. Varying with the number of the chemical species appeared, as well as of the reactions between them, sometimes with a high level of complexity, constituted in a system, a high number of independent chemical reactions can occur.

In such circumstances, the traditional studies, strictly bounded by the processes' chemistry become insufficient. The classical solution, helped by the Le Châtelier principle, does not offer answers for the systems formed out of more constituents. As a result, for such situations, methods of numeric calculating have been initiated, achievable only by super powerful computers.

The calculation has been based on generalizing physical-chemical ideas.

Referring to the method of chemistry constants, improved [2-3], of there will be an emphasis on the methodology of modeling adapted to the specific of each given reactions system (the applied method is a general and flexible).

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The systems will be solved with application packages " Mathlab ", for systems of non linear equations, and the graphical representations will be realized basing on applications packages Microsoft Office – " Excel ".

Methodology of calculations

The purpose of the paper is to calculate the concentrations of the chemical species from the electrolytes solutions.

The starting point is the essential observation that in the final equilibrium status – regardless the interactions between the processes by the common chemical species – the concentrations of all the species will be constant; this status is called *stationary status.* The applications are for an ideal case, regardless the activity factors.

The general methodology applied for calculations was the equilibrium constant method, improved. We can calculate the chemical species concentrations for solutions: weak polybasic acids; salts formed of weak polybasic acids and strong bases (the salts of phosphoric acid); buffer solutions; solutions obtained by combining an acid and a base. In order to underline the modeling method, a particular case is exemplified.

To calculate the molar concentration of the chemical species of a solution of NaH_2PO_4 in a concentration 0,1 M, the serie of possible simultaneous reactions is [4-5]:

R_1: $H_2O + H_2O = H_3O^+ + HO^-$

R_2: $H_2PO_4^- + H_2O = H_3PO_4 + HO^-$

R_3: $H_2PO_4^- + H_2O = HPO_4^{2-} + H_3O^+$

R_4: $HPO_4^{2-} + H_2O = PO_4^{3-} + H_3O^+$

R_5: $HPO_4^{2-} + H_2O = H_2PO_4^- + HO^-$

R_6: $H_3PO_4 + H_2O = H_2PO_4^- + H_3O^+$

To establish the maximum number of independent formally possible reactions between the chemical species in the solution, the atomic matrix, **A**, is formed, its data being presented in the table 1:

Table 1. The atomic matrix

	Na^+	HO^-	H_3O^+	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}	H_3PO_4	H_2O
b_{Na}	1	0	0	0	0	0	0	0
b_H	0	1	3	2	1	0	3	2
b_P	0	0	0	1	1	1	1	0
b_O	0	1	1	4	4	4	4	1

(b_{Na}, b_H, b_P, b_O represents the total number of atoms – gram from the atomic species Na, H, P, O, present in the system chemical species).

The maximum number of independent formal possible relations is equal to the difference between the number of the components from the chemical homogeneous system and the rank of the atomic matrix 8 – 4 = 4 [6].

Let **R** be the stoechiometric matrix of reactions R_1, R_2, R_3, R_4, R_5, R_6 (matrix R is formed out of the stoechiometric coefficients values of chemical system substances after all the reactions substances were passed into the right side, the stoechiometric coefficients of reacting substances being affected with the minus sign). The table for the stoechiometric matrix **R** is:

Table 2. The stoechiometric matrix of reactions R_1, R_2, R_3, R_4, R_5, R_6

	Na^+	HO^-	H_3O^+	$H_2PO_4^-$	HPO_4^{2-}	PO_4^{3-}	H_3PO_4	H_2O
R_1	0	1	1	0	0	0	0	-2
R_2	0	1	0	-1	0	0	1	-1
R_3	0	0	1	-1	1	0	0	-1
R_4	0	0	1	0	-1	1	0	-1
R_5	0	1	0	1	-1	0	0	-1
R_6	0	0	1	1	0	0	-1	-1

From the above-presented reactions we choose a maximal set of independent reactions as it follows: we calculate the rank of matrix **R** and we establish the main determinant. The reactions, which correspond to the lines of which the main determinant is formed, are a maximal set of independent reactions. The maximum possible rank of the matrix is 4. The main determinant was considered the determinant formed with the stoechiometric coefficients of the species HO^-, H_3O^+, $H_2PO_4^-$, HPO_4^{2-} from the reactions R_1, R_2, R_3, R_4. The matrix corresponding to the 4 chemical reactions has the rank 4.

The four reactions of equilibrium will be chosen so that they should contain the dissociation reactions of the acids in the system and the water dissociation reactions.

The water is in large quantity, therefore its concentration is considered to be constant. The concentration of the Natrium ion is equal to the molar concentration of the salt.

To calculate the concentration of all the other chemical species (of the species HO^-, H_3O^+, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, H_3PO_4) there are to be written:

I. Relations between concentrations expressed with the law of masses, using the equlibrium constants that we know, for each independent equilibrium.

II. The relation of charge conservation: the sum of the system cautions charge is equal to the sum of anions charges.

III. Relations of initial quantities (moles) conservation.

We added two lines, which correspond to the charge conservation relations and to the initial quantities [7], in matrix formed with the stoechiometric coefficients of the species HO^-, H_3O^+, $H_2PO_4^-$, HPO_4^{2-} from the reactions R_1, R_2, R_3, R_4. This matrix rank is 6, so we have 6 independent chemical reactions.

Let $[HO^-]$ = a; $[H_3O^+]$ = b; $[H_2PO_4^-]$ = c; $[HPO_4^{2-}]$ = d; $[PO_4^{3-}]$ = e; $[H_3PO_4]$ = f; $[Na^+]$ = 0.1 mol/L - the concentration of chemical species and $K_{HPO4}{}^{2-} = 10^{-12}$ moles/L; $K_{H2PO4}{}^{-} = 6.2 * 10^{-8}$ moles/L; $K_{H3PO4} = 5.9 * 10^{-3}$ moles/L; $K_{H2O} = 10^{-14}$ moles^2/L^2 the equlibrium constants, for each independent equilibrium.

Solving the 6 mathematical equations:

$a * b = 10^{-14}$

$a * f / c = 10^{-14} / 5.9 * 10^{-3}$

$b * d / c = 6.2 * 10^{-8}$; $b * e / d = 10^{-12}$

$b + 0.1 = a + c + 2*d + 3*e$

$0.1 = c + d + e + f$

we obtain the concentrations of chemical species present in monosodium phosphate 0,1M.

[a,b,c,d,e,f] = solve('a*b=10^(-14)','a*f/c=10^(-14)/(5.9*10^(-3))','b*d/c=6.2*10^(-8)','b*e/d=10^(-12)','b+0.1=a+c+2*d+3*e','0.1=c+d+e+f','a>0')

Solution:

a = .5381510687e-9; $[HO^-] = 5.381510 * 10^{-10}$ mol/L

b = .1858214279e-4; $[H_3O^+] = 1.858214 * 10^{-5}$ mol/L

c = .9935557452e-1; $[H_2PO_4^-] = 9.935557 * 10^{-2}$ mol/L

d = .3315035134-3; $[HPO_4^{2-}] = 3.315035 * 10^{-4}$ mol/L

e = .1783989700e-10; $[PO_4^{3-}] = 1.783989 * 10^{-11}$ mol/L

f = .3129219444e-3; $[H_3PO_4] = 3.129219 * 10^{-4}$ mol/L

By solving the chemical system, initiated with different molar concentrations for NaH_2PO_4 the six substances concentrations belong to the equilibrium homogeneous system were obtained.

Observation

The independent chemical reactions will generally be chosen so that they should contain the ionizing reactions of the acid and the ionizing reaction of water.

Water based solution of a salt (or a salt mixture) is mathematically calculable as if we had in the solution the acid and base out of which the salt came was obtained [8].

Results and discussions

Based on the processed calculations (table 3) it is discussed the influence of the type and of the salt concentration on the chemical species concentrations in an equilibrium status.

Table 3. The chemical species concentration in the equilibrium

Electrolyt	Electrolyt concentration	$[HO^-]$	$[H_3O^+]$	$[H_2PO_4^-]$	$[HPO_4^{2-}]$	$[PO_4^{3-}]$	$[H_3PO_4]$
	0,1 M	5,38E-10	1,86E-05	9,94E-02	3,32E-04	1,78E-11	3,13E-04
NaH_2PO_4	0,2 M	5,31E-10	1,88E-05	1,99E-01	6,54E-04	3,47E-11	6,35E-04
	0,3 M	5,28E-10	1,89E-05	2,98E-01	9,76E-04	5,15E-10	9,57E-04
	0,1 M	3,83E-05	2,61E-10	4,18E-04	9,92E-02	3,80E-04	1,85E-11
Na_2HPO_4	0,2 M	3,92E-05	2,55E-10	8,17E-04	1,98E-01	7,77E-04	3,53E-11
	0,3 M	3,95E-05	2,53E-10	1,22E-03	2,98E-01	1,18E-03	5,21E-11
	0,1 M	2,70E-02	3,70E-13	1,61E-07	2,70E-02	7,30E-02	1,01E-17
Na_3PO_4	0,2 M	4,00E-02	2,50E-13	1,61E-07	4,00E-02	1,60E-01	6,80E-18
	0,3 M	5,00E-02	2,00E-13	1,61E-07	5,00E-02	2,50E-01	5,47E-18

We can notice in the table 3 that for all salts, the chemical species with maximum concentration in the equilibrium is the one resulted from the ionizing the salt and increases by the same number of times as the salt concentration (table 4):

Table 4. Change of the chemical species with maximum concentration in the equilibrium with the salt concentration

Compound	Concentration	0,001	0,01	0,1	0,2	0,3
$[NaH_2PO_4]$	$[H_2PO_4^-]$	9,9E-4	9,9E-05	9,94E-02	1,99E-01	2,98E-1
$[Na_2HPO_4^-]$	$[HPO_4^{2-}]$	9,8E-4	9,9E-03	9,92E-02	1,98E-01	2,98E-1

The solution pH increase as the solutions dilution increases for NaH_2PO_4 and decreases for Na_2HPO_4.

Table 5. Change of the solution pH with the dilution increases

Concentration	0,001	0,01	0,1	0,2	0,3
$[NaH_2PO_4]$	5,13	4,82	4,73	4,725	4,723
$[Na_2HPO_4]$	9,08	9,46	9,58	9,59	9,60

Once increasing the salt concentration for 1, 2, 3 times, the concentrations of the chemical species which contain phosphor ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, H_3PO_4) increase the same number of times.

Discussions may go on, making the initial conditions more complicated.

Many of the reactions that occur in living organisms are extremely sensitive to the ph of reaction environment. In order to keep the pH constant in internal environment, the human organism uses the acids and bases neutralizing by the buffer solution; the renal elimination of the acids which are in excess, the functional elimination of CO_2, the most frequent product of the organism. The most important buffer systems, which work in the human body, are H_2CO_3 / HCO_3^-, $H_2PO_4^-$ / HPO_4^{2-}.

We can calculate, for instance, the report in which the acid phosphates are mixed in order to obtain a buffer system having a pH = 7,4, equal to the blood pH. The initial concentration of NaH_2PO_4 is 0,1 moles/L and the initial concentration of Na_2HPO_4 is 0,1*r moles/L, the value for “r” is obtained, is 1,56.

Conclusions

The calculation methods of the chemical equilibrium in multi-compound systems are not limited to the presented situation. They are general and we are able to apply them to more and more complex systems, contrasting to the traditional calculation methods which do provide complete ways of solving but in simple situations or which can be simplified for isolated cases.
We can calculate the composition within an equilibrium status for: equilibria for precipitation, involving complex combinations formation, equilibria involving an electrons exchange, etc.
This paper presents in systematical and carefully detailed way, the ways of approaching such complex systems, in order to establish out the composition in an equilibrium status.

Finally, some mentions regarding the adopted simplifications have been made:

- the hypothesis of the ideality
- some aspects concerning the inconvergence of the algorithm determined by substances present in small concentrations
- approximation errors in computer
- the selection of initial mathematical approximation and so on.

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