Proceedings of the 24th International Symposium "The Environment and the Industry"
(E-SIMI 2021), 24 September 2021, online event

pH-metric method determining the solubility and solubility products of slightly soluble salts of arbitrary composition

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Abstract
The developed method of determining K_S from pH metric data has a number of advantages compared to those used traditionally. First, in place of the residual concentrations of the salt components, only the pH value of the saturated solution is used in the derived expressions. Thus, the number of independent variables, which need to be measured experimentally, is reduced. Furthermore, the potentiometric method, used to determine the pH, is sufficiently accurate, simple and universal and does not necessitate the use of ion-selective electrodes. At the same time, the residual concentrations are usually measured by chemical methods, which are inferior in most cases, for several reasons, compared to the potentiometric method. Second, the K_S value calculated by the developed method has a thermodynamic character. The organization of the experiment must be appropriate to the applied equations. Therefore, it is necessary to draw attention to the need for high accuracy in the process of preparing the initial solutions, because the initial concentrations of the precipitate components are included in the calculation formulas. The developed method for determining Ks can be applied for systems of any degree of complexity, which contain additional complexing agents.

Keywords: residual concentration, slightly soluble salts, solubility, solubility products, thermodynamic modeling

INTRODUCTION

The solubility product is an important feature in estimating the thermodynamic properties of substances and is widely used to create optimal schemes for compound synthesis and technological treatment of aqueous-saline systems [1-4]. The solubility product K_S of a salt of arbitrary composition $M_mA_{n(S)}$ (where M^{n+} is the metal ion and A^{m-} - the salt anion)

$$K_S = [M^{n+}]^m[A^{m-}]^n, \qquad (1)$$

([i] denotes the equilibrium concentration of the ion „i") is the equilibrium constant of the reaction
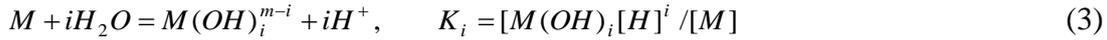
$$M_mA_{n(S)} = mM^{n+} + nA^{m-}. \qquad (2)$$

The product of activity is a thermodynamic constant, analogous to (1), in which instead of equilibrium concentrations there are ion activities:

$$K_S^0 = a_M^m a_A^n.$$

To determine the size of K_S (or K_S^0) it is necessary to measure, in principle, the concentrations (or activities) of the salt cation and anion. At the same time, there are certain difficulties in the determination of K_S when mixing the reagents, because concomitantly with the basic precipitation-

dissolution reaction (2) other secondary reactions of the salt components with water dissociation products take place (species charges, as usual, are omitted):

$$M + iH_2O = M(OH)_i^{m-i} + iH^+, \qquad K_i = [M(OH)_i[H]^i / [M] \tag{3}$$

$$A + jH = H_jA, \quad K_j = \frac{[H_jA]}{[H]^j[A]} \tag{4}$$

neglect of which frequently presents a considerable source of error [5].

In this paper original equations for K_S calculation are developed, based on data on the residual concentration of one of the solid phase ions, and under the conditions of reactions (3) or (4), only based on the pH value of the saturated solution [6, 7].

RESULTS AND DISSCUTION

Within the residual concentration (*RC*) method the conditions of the mass balance in the heterogeneous system (2) - (4) have the form:

$$C_M^0 = \Delta C_M + C_M^r \tag{5}$$

$$C_A^0 = \Delta C_A + C_A^r \tag{6}$$

where $\Delta C_i = n_i / V$, n is the amount of the "*i*" ion in the precipitate and *V* is the volume of solution. In the last two equations with top indices „*0*" and „*r*" the initial concentration of the salt ion in the mixture and its residual concentration in the solution are noted respectively. Residual concentrations can be represented by expressions [8]:

$$C_M^r = \sum_{i=0}[M(OH)_i = [M]\left(1 + \sum_{i=1}K_i[H]^{-i}\right) = [M]\alpha_M \tag{7}$$

$$C_A = \sum_{j=0}[H_jA] = [A]\left(1 + \sum_{j=1}K_j[H]^j\right) = [A]\alpha_A.$$

In writing the last two equations, the consequences of the law of mass action (3) and (4) were used:

$$[M(OH)_i] = K_i[M][H]^{-I} \qquad\qquad [H_jA] = K_j[A][H]^j.$$

By α_i the coefficients of the secondary reactions of the precipitate ions (3) and (4) are noted. From the stoichiometry of the solid phase, one gets

$$m\Delta C_A = n\Delta C_M \tag{8}$$

Further, the ratio of the initial concentrations is noted by

$$k = C_A^0 / C_M^0 \tag{9}$$

which is known in the process of preparing the mixture.

Then, subtracting equation (5) from (6), with evidence (8) and (9), one obtains

$$(mk - n)C_M^0 = m[A]\alpha_A - n[M]\alpha_M = mC_A^r - nC_M^r. \tag{10}$$

Equation (10) allows the estimation of the reciprocal link and the agreement between the experimental data C_A^r and C_M^r. Failure of the correlation (10) can serve as an evidence of the transformation of one solid phase to another. Given that according to (1)

$$[A] = K_S^{1/n}[M]^{-m/n},$$

equation (10) is rewritten in the form:

$$mK_S^{1/n}[M]^{-m/n}\alpha_A = n[M]\alpha_M + (mk - n)C_M^0,$$

whence it follows, that

$$K_S = \left(\frac{n[M]\alpha_M + (mk - n)C_M^0}{m\alpha_A}\right)^n [M]^m.$$

Finally, after the given expression has been logarithmic, result the following relation:

$$\log K_S = n\log\left[n[M]\alpha_M + (mk - n)C_M^0\right] - n\log(m\alpha_A) + m\log[M]. \tag{11}$$

Similarly, given the relationship

$$[M] = K_S^{1/m}[A]^{-n/m},$$

the following result is reached:

$$\log K_S = m\log\left[m[A]\alpha_A - (mk-n)C_M^0\right] - m\log(n\alpha_M) + n\log[A]. \tag{12}$$

Based on equations (11) and (12) the K_S value is calculated from the measured equilibrium concentration of one of the salt components and the pH of the given solution, knowing the tabular values K_i and K_j. By measuring, the activity of one of the precipitate ions and using equilibrium thermodynamic constants K_S^0 was obtained. Three extreme situations will be analysed, which are frequently encountered in practice, when the equations deduced above are considerably simplified.

I. In acidic environments the hydrolysis of many metal ions can be neglected, i.e. $\alpha_M \cong 1$. Then the equations of K_S calculation were simplified:

$$\log K_S = n\log\left[n[M] + (mk-n)C_M^0\right] - n\log(m\alpha_A) + m\log[M]$$
$$\log K_S = m\log\left[m[A]\alpha_A - (mk-n)C_M^0\right] - m\log n + n\log[A].$$

II. In alkaline environments the anion is usually completely deprotonated and $\alpha_A \cong 1$.

$$\log K_S = n\log\left[n[M]\alpha_M + (mk-n)C_M^0\right] - n\log m + m\log[M]$$
$$\log K_S = m\log\left[m[A] - (mk-n)C_M^0\right] - m\log(n\alpha_M) + n\log[A]$$

III. In the absence of side effects (35) and (36) yields

$$\log K_S = n\log\left[n[M] + (mk-n)C_M^0\right] - n\log m + m\log[M]$$
$$\log K_S = m\log\left[m[A] - (mk-n)C_M^0\right] - m\log n + n\log[A]$$

If the initial concentrations of the precipitate components are taken in stoichiometric ratio, i.e. $nC_M^0 = mC_A^0$, then $k = n/m$ and already known relationships are obtained [9]:

$$K_S = \left(\frac{n}{m}\right)^n [M]^{m+n}, \qquad K_S = \left(\frac{m}{n}\right)^m [A]^{m+n},$$

corresponding to the condition $m[A] = n[M]$. It is necessary to mention that the deduced relations can be used for the calculation of the constants K_i (K_j) for the known values K_S and K_j (K_i) according to approved methods [10].

Under the conditions of the secondary reactions (3) and (4), an additional MB equation can be formulated:

$$C_H^0 = [H] - [OH] + \sum_{j=1} j[H_jA] - \sum_{i=1} i[M(OH)_i] = [H] - [OH] + [A]\sum_{j=1} jK_j[H]^j - [M]\sum_{i=1} iK_i[H]^{-i} \tag{13}$$

From here, for the equilibrium concentration of the anion, the following expression is obtained

$$[A] = \frac{1}{\sum\limits_{j=1} jK_j[H]^j}\left(C_H^0 - [H] + [OH] + [M]\sum_{i=1} iK_i[H]^{-i}\right). \tag{14}$$

On the other hand, it follows from equation (10)

$$[A] = \frac{1}{m\alpha_M}\left((mk-n)C_M^0 + n[M]^m\right) \tag{15}$$

By comparing equations (14) and (15), after some changes, it appears

$$[M] = \frac{(mk-n)C_M^0 \sum\limits_{j=1} jK_j[H]^j - m\alpha_M\left(C_H^0 - [H] + [OH]\right)}{m\alpha_M \sum\limits_{i=1} iK_i[H]^{-i} - n\alpha_M \sum jK_j[H]^j}. \tag{16}$$

Therefore, calculating $[M]$ according to equation (16) and then $[A]$ from equation (15), one gets $K_S = [M]^m[A]^n$. This method allows the calculation of K_S only from the value $pH = -\log a_{H^+} = -\log[H^+]f_H$. Two possible extreme situations will be examined:

1. In the absence of protonation reactions ($\alpha_A \cong 1$)

$$[M] = \frac{[H] - C_H^0 - [OH]}{\sum\limits_{i=1} iK_i[H]^{-i}}, \qquad [A] = \frac{1}{m}\left[(mk-n)C_M^0 + n[M]\alpha_M\right] \tag{17}$$

2. If the metal ion is not hydrolysed, then

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$$[M] = \frac{m}{n}\left[\frac{(C_H^0 - [H] + [OH]\alpha_A)}{\sum\limits_{j=1}^{r} jK_j[H]^j} - \left(k - \frac{n}{m}\right)C_M^0\right] \qquad (18)$$

$$[A] = \frac{1}{m}\left[(mk - n)C_M^0 + n[M]\right].$$

It should be mentioned here that equations (16) - (18) are valid only in case of at least one of the side reactions (3) or (4). The developed method was successfully applied to the K_S determination of a series of salts.

As an example of the use of the equations obtained for the calculation of K_S, the system „$La(NO_3)_3 - H_3PO_4 - H_2O$" will be examined. Experimental data and calculation results, obtained by Tananaev [11], but also the results of our calculations are presented in Table 1. The solubility product of $LaPO_{4(S)}$ was calculated according to equations (11) and (12), which in this case have the form:

$$\log K_S = \log\left[C_{La}^r + (k-1)C_{La}^0\right] - \log(\alpha_{PO_4}) + \log C_{La}^r, \quad (A)$$

$$\log K_S = \log\left[C_{PO_4}^r - (k-1)C_{La}^0\right] - \log(\alpha_{La}) + \log C_{PO_4}^r \quad (B)$$

where

$$\alpha_{PO_4} = 1 + K_{HPO_4}[H] + K_{H_2PO_4}[H]^2 + K_{H_3PO_4}[H]^3.$$

In the pH-examined range $C_{La}^r = [La^{3+}]$ $(\alpha_{La} = 1)$. For the rectification of the non-ideality of the system, the equations of the dependence of the constants of dissociation of H_3PO_4 on ionic strength I $(I \leq 4)$ were used [8]:

$$pK_1^D = pK_1^{D(0)} - \frac{I^{1/2}}{1 + \alpha_1 I^{1/2}} + B_1 I$$

$$pK_2^D = pK_2^{D(0)} - \frac{2I^{1/2}}{1 + \alpha_2 I^{1/2}} + B_2 I$$

$$pK_3^D = pK_3^{D(0)} - \frac{3I^{1/2}}{1 + \alpha_3 I^{1/2}} + B_3 I.$$

Here $pK_1^{D(0)} = 2.172$; $pK_2^{D(0)} = 7.211$; $pK_3^{D(0)} = 12.360$.

The following empirical coefficients were used: $\alpha_1 = 0.926$, $B_1 = 0.1560$; $\alpha_2 = 1.181$, $B_2 = 0.1591$; $\alpha_3 = 1.268$, $B_3 = 0.1835$.

From these equations the constants of species formation were calculated for different values of the ionic strength, taking into account that

$$\log K_{HPO_4} = pK_3^D; \quad \log K_{H_2PO_4} = pK_3^D + pK_2^D; \quad \log K_{H_3PO_4} = pK_3^D + pK_2^D + pK_1^D.$$

The activity product was calculated from *Davies*' equation:

$$\log K_S^0 = \log K_S - (m+n)(z_M Z_A)A_D\left(\frac{I^{1/2}}{1 + I^{1/2}} - 0.3I\right) \quad (C)$$

Here $A_D = 0.5091$, $m = n = 1$, $z_M = z_A = 1$, $z_M = 3$ and $z_A = 3$.

The results of the K_S and K_S^0 determination performed by the author [11] and our calculations are presented in Table 2. The comparison of the K_S values from the data (C_{La}^r, pH) and $(C_{PO_4}^r, pH)$, but also equation (10) allows to pronounce about the accuracy of the latter. Thus, for $n = 0.90$ the measured values $C_{PO_4}^r$ are obviously diminished. These results correlate well with the literature data [11], if at the same time it is taken into account that the method of highlighting the non-ideality of the system in the cited paper is not known.

According to the authors, for the calculation of K_S instead of the data set $(C_{La}^r, C_{PO_4}^r, pH)$, preference should be given to data (C_{La}^r, pH) or $(C_{PO_4}^r, pH)$, depending on the accuracy and security

of the measurement method of C_i^r. In addition, for the examined conditions, it is better to use the data (C_{La}^r, pH) because the anion PO_4^{3-} participates in complexation reactions (3).

Therefore, the obtained equations allow the calculation of K_S from the experimental data (C_{La}^r, pH) and $(C_{PO_4}^r, pH)$ for the precipitate of a known composition provided that the stability constants of the complex species formed are known. In the case of the formation or predominance of one of the complex species, its formation constant can be easily calculated based on the known K_S value and the experimental data obtained using the RC method.

In order to verify the usefulness of equations (16) and (18) for the calculation of K_S, the system „GdCl$_3$ – H$_3$PO$_4$ – H$_2$O" was studied. The experimental data and the calculation results, obtained by Denisova [12], but also our results are presented in Table 3. Equations (18) in this case have the form (within the pH range $1.5 \div 2.0$ hydroxyl ions can be neglected, therefore $[OH] \cong 0$):

$$[Gd^{3+}] = \frac{(3kC_{Gd}^0 - [H])\alpha_{PO_4}}{K_1[H] + K_2[H]^2 + 3K_3[H]^3} - (k-1)C_{Gd}^0,$$

$$[PO_4^{3-}] = \frac{(k-1)C_{Gd}^0 + [Gd^{3+}]}{\alpha_{PO_4}}.$$

As one can see, the results of the K_S calculation based only on the measured pH value of the saturated solution practically coincide with the results of the calculation based on C_{Gd}^r and $C_{PO_4}^r$.

The organization of the experiment must be appropriate to the applied equations. Therefore, it is necessary to draw attention to the need for high accuracy in the process of preparing the initial solutions, because the initial concentrations of the precipitate components are included in the calculation formulas.

It is useful to note that the proposed method for determining K_s can be developed for systems of any degree of complexity, which contain additional complexing agents.

Table 1. The results of the system analysis „La(NO$_3$)$_3$ – H$_3$PO$_4$ – H$_2$O",
t = 25 °C, $C_{La}^0 = 0.025$ mol/L [11]

k	C_{La}^0, mol/L	$C_{PO_4}^0$, mol/L	pH
0.50	0.0128	0.00118	1.95
0.90	0.0070	0.005	1.80
1.00	0.00592	0.00636	1.70
1.25	0.00265	0.00896	1.67
1.50	0.00214	0.0139	1.65
2.00	0.00132	0.0255	1.65
2.50	0.000636	0.0380	1.65

Table 2. The results of the calculation of the solubility product K_S^0 of the system„ La(NO$_3$)$_3$ – H$_3$PO$_4$ – H$_2$O". t = 25 °C, $C_{La}^0 = 0.025$ mol/L [11]

k	I	pK_S[13]	pK_S^*	pK_S^{**}	pK_S^0 [13]	pK_S^{0*}	pK_S^{0**}
0.50	0.102	19.92	19.32	19.65	21.91	21.26	21.59
0.90	0.079	20.03	19.62	18.50	21.86	21.41	20.29
1.00	0.077	20.29	20.07	20.01	22.10	21.85	21.79
1.25	0.064	20.63	20.40	20.38	22.34	22.07	22.05
1.50	0.063	20.60	20.33	20.54	22.28	22.00	22.21
2.00	0.061	20.55	20.30	20.73	22.22	21.95	22.38
2.50	0.058	20.77	20.47	20.58	22.33	22.09	22.22

*: calculation according to the equation (A);
**: calculation according to the equation (B).

It is obvious that in the case of slightly soluble basic $M_m(OH)_xA_{y(S)}$ and acidic $M_mH_xA_{y(S)}$ salts such equations become more complicated, because the number of components in the precipitate increases.

Table 3. The results of the analysis and calculation of K_S^0 for the system „$GdCl_3 - H_3PO_4 - H_2O$".
t = 25 °C, $C_{Gd}^0 = 0.025$ mol/L ($C_H^0 = 3C_{PO_4}^0 = 3kC_{Gd}^0$).

k	pH	C_{Gd}^r, mol/L	$C_{PO_4}^r$, mol/L	pK_S [12]	pK_S (our calculations)
		Analysis		The results of the calculation	
0.50	1.91	0.0147	0.00107	19.97	19.88
1.00	1.60	0.0064	0.0062	20.51	20.54
1.50	1.54	0.0033	0.0154	20.62	20.50
2.00	1.50	0.0022	0.0272	20.67	20.48
2.50	1.50	0.0017	0.0390	20.64	20.34

The process of precipitation-dissolution of a slightly soluble acid salt with a known composition $M_mH_xA_{y(S)}$ in saturated aqueous solution can be presented by means of the equations:

$$M_mH_xA_{y(S)} = mM + xH + yA, \quad K_S^H = [M]^m[H]^x[A]^y, \tag{19}$$

$$M + iH_2O = M(OH)_i^{m-i} + iH^+, \quad K_i = [M(OH)_i][H]^i / [M] \tag{20}$$

$$A + jH = H_jA, \quad K_j = \frac{[H_jA]}{[H]^j[A]}. \tag{21}$$

The last two equations take into account the side effects of the precipitate components. Species charges for simplicity were omitted. Next to the reaction, equations are written the expressions for the respective equilibrium constants. The conditions of the mass balance (MB) in terms of the amount of substance m (in moles) for systems (19) to (21) are as follows:

$$m_M^0 = \Delta m_M + m_M^r, \quad m_A^0 = \Delta m_A + m_A^r, \quad m_H^0 = \Delta m_H + m_H^r, \tag{22}$$

where $m_i^0, \Delta m_i, m_i^r$ denotes respectively the amount of ion in the precipitate, in the volume of the mixture and in the volume of the liquid phase of the mixture (in solution). From the stoichiometry of the precipitate $M_mH_xA_{y(S)}$ it follows that

$$y\Delta m_M = m\Delta m_A, \quad x\Delta m_M = m\Delta m_H, \quad y\Delta m_H = x\Delta m_A. \tag{23}$$

The ratio of the initial quantities of ions in the mixture will be noted by:

$$m_A^0 / m_M^0 = n \quad \text{and} \quad m_H^0 / m_M^0 = q \tag{24}$$

In connection with the relations (23) it is necessary to mention that they are valid only under the conditions of precipitation of a compound of the indicated composition. If two or more solid phases are formed, in other words, a precipitate of variable composition is obtained from the mixture of several individual substances in different ratios, equation (23) loses its meaning.

According to the methodology described in our previous paper [14], following the linear combinations of relations (23), equations were deduced, in which the terms Δm_i were excluded:

$$\left(n - \frac{y}{m}\right)m_M^o = m_A^r - \frac{y}{m}m_M^r,$$

$$\left(q - \frac{x}{m}\right)m_M^0 = m_H^r - \frac{x}{m}m_M^r, \tag{25}$$

$$\left(q - \frac{nx}{y}\right)m_M^0 = m_H^r - \frac{x}{y}m_A^r.$$

Dividing by the volume of the liquid phase (solution), proceed to concentrations:

$$\left(n - \frac{y}{m}\right)C_M^0 = C_A^r - \frac{y}{m}C_M^r,$$

$$\left(q - \frac{x}{m}\right)C_M^0 = C_H^0 - \frac{x}{m}C_M^r, \tag{26}$$

In most cases, the volume of the liquid phase practically does not differ from the volume of the mixture, especially for dilute solutions [8, 14].

$$\left(q - \frac{nx}{y}\right)C_M^0 = C_H^r - \frac{x}{y}C_A^r. $$

Then, the residual concentrations of the components were expressed by the equilibrium concentrations and the equilibrium constants of the reactions (20)-(21):

$$C_M^r = \sum_{i=0}[M(OH)_i] = [M]\left(1 + \sum_{i=1}K_i[H]^{-i}\right) = [M]\alpha_M, \tag{27}$$

$$C_A = \sum_{j=0}[H_jA] = [A]\left(1 + \sum_{j=1}K_j[H]^j\right) = [A]\alpha_A. \tag{28}$$

$$C_H^0 = [H] - [OH] + \sum_{j=1}j[H_jA] - \sum_{i=1}i[M(OH)_i] = [H] - [OH] + [A]\sum_{j=1}jK_j[H]^j - [M]\sum_{i=1}iK_i[H]^{-i}. \tag{29}$$

In the last equation the expression of the ionic product of water $K_w = [H][OH]$ was used. Based on the relations (26), after a series of transformations, taking into account (27) - (29), the desired equations for the calculation of the equilibrium concentrations of the cation and the anion are determined:

$$[M] = \frac{\left(C_M^0(q - x/m) + [OH] - [H]\right)\alpha_A + C_M^0(y/m - n)\sum_{j=1}jK_j[H]^j}{\dfrac{y}{m}\sum_{j=1}jK_j[H]^j - \alpha_A\sum_{i=1}iK_i[H]^{-i} - \dfrac{x}{m}\alpha_M\alpha_A}, \tag{30}$$

$$[A] = \frac{\left(n - \dfrac{y}{m}\right)C_M^0 + \dfrac{y}{m}[M]\alpha_M}{\alpha_M}. \tag{31}$$

As can be seen, equations (29) - (31) allow the calculation of the equilibrium concentrations of the precipitate ions based only on the experimental pH values of the saturated salt solution. In the absence of side effects these equations are considerably simplified:

$$[M] = \frac{m}{x}\left[C_M^0\left(\frac{x}{m} - q\right) + [H] - [OH]\right],$$

$$[A] = \left(n - \frac{y}{m}\right)C_M^o + \frac{y}{m}[M]. \tag{32}$$

After determining [M] and [A] the solubility product of the basic salt can be calculated according to equation (19). Residual cation and anion concentrations are found using (27) and (28). Then, the degree of precipitation of the salt can be determined by the equation

$$\gamma = \frac{C_M^0 - C_M^r}{C_M^0} = \frac{\Delta C_M}{C_M^0}.$$

The following are also the main results and their analysis in case of formation of a slightly soluble basic salt $M_m(OH)_xA_{y(S)}$ according to the scheme:

$$M_m(OH)_xA_{y(S)} = mM + xH_2O + yA, \qquad K_S^{OH} = [M]^m[H]^{-x}[A]^y,$$
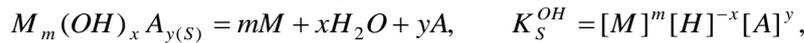
with evidence of reactions (20) - (21). The MB conditions in respect of cation and anion remain the same (equations (27)-(28)). In the case of the excess of hydroxyl ion, it can be written [8, 15]

$$m_{OH}^0 = \Delta m_{OH} + m_{OH}^r.$$

The "stoichiometric" relations $x\Delta m_M = m\Delta m_{OH}$, $y\Delta m_{OH} = x\Delta m_A$ are taken into account. After a series of transformations, analogous to the previous case, it is obtained definitively in terms of concentrations:

$$(mn - y)C_M^0 = mC_A^r - yC_M^r,$$
$$(km - x)C_M^0 = mC_{OH}^r - xC_M^r, \tag{33}$$

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$$(ky-nx)C_M^0 = yC_{OH}^r - xC_A^0,$$

where $k = \dfrac{m_{OH}^0}{m_M^0}$.

In the absence of side reactions (20) - (21), it is obtained

$$C_{OH}^r = [OH] - [H],$$

$$C_M^r = \frac{m}{x}C_{OH}^r - \left(\frac{km}{x}-1\right)C_M^0, \tag{34}$$

$$C_A^r = \frac{y}{x}C_{OH}^r - \left(\frac{ky}{x}-n\right)C_M^r.$$

As an illustration of the practical application of the equations deduced, two concrete systems will be examined.

System „ Y(NO₃)₃ – H₄L – H₂O" where L^{4-} is the anion of aminobenzylidene-diphosphonic acid. Following the research of this system, Tereshin et al established the formation of a precipitate of variable composition, in which the ratio of ligand to yttrium is equal to 1 in the ranges of n values from 0.5 to 1.0 and then increases to 3.35 with increasing value of n to 3 [16]. The analysis showed that the precipitate of variable composition as an individual phase contains acid.
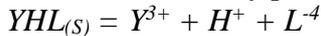
For $n = C_L^0 / mC_y^0 = 1$, $C_y^0 = 0.01$ mol/L, the measured value of $[H^+]$ of saturated solution at room temperature is equal to $2.94 \cdot 10^{-2}$ mol/L. For the given value $[H^+]$ $\alpha_Y = 1$, and α_L was calculated according to the equation:

$$\alpha_L = 1 + \sum_{j=1} K_j [H]^j,$$

Here $\log K_1 = 10.29$, $\log K_2 = 18.46$, $\log K_3 = 23.75$, $\log K_4 = 25.35$ [17]. For $n=0$ the equations (30) and (31) take the form, $q = 4 \cdot n = 4$:

$$[Y] = \frac{\left(3C_Y^0 - [H]\alpha_L\right)}{K_2[H]^2 + 2K_3[H]^3 + 3K_4[H]^4}, \quad [L] = \frac{[Y]}{\alpha_L}.$$

Then the reaction solubility product:

$$YHL_{(S)} = Y^{3+} + H^+ + L^{-4}$$

is equal to

$$K_S = [Y][H][L] = \alpha_L[H]\frac{\left(3C_y^0 - [H]\right)^2}{K_2[H]^2 + 2K_3[H]^3 + 3K_4[H]^4} = 5.29 \cdot 10^{-29}.$$

The obtained value practically coincides with the geometric value $pK_S = -\log K_S = 28.3$, calculated in [15], being based on C_Y^r and C_L^r.

System "CeCl₃ – NaOH – H₂O"

Tananaev and Bokmelder demonstrated that the interaction of cerium (III) chloride with sodium hydroxide gives the basic salt $Ce(OH)_2Cl$, which at the subsequent interaction with the alkaline base is converted to hydroxide [18]. The obtained data based on the residual concentrations method are presented in Tables 4 and 5. It was found that at $k = C_{OH}^0 / C_{Ce}^0 = 2.5$ all Ce^{3+} is in the precipitate in the form of basic salt. Within the range of $2.5 < k < 3.0$ the precipitate presents a mixture of basic salt and hydroxide. The same tables show the results of the calculations of the residual concentrations C_{Ce}^r and C_{Cl}^r based on equations 66 which have the form $(n = C_{Cl}^0 / C_{Ce}^0 = 3)$:

$$C_{Ce}^r = \frac{1}{n_S^{OH}}\left(K_w[H]^{-1} - [H] - (k - n_S^{OH})C_{Ce}^0,\right)$$

$$C_{Cl}^r = \frac{n_S^{Cl}}{n_S^{OH}}\left(K_w[H]^{-1} - [H]\right) - \left(k\frac{n_S^{Cl}}{n_S^{OH}} - 3\right)C_{Ce}^0.$$

Here $n_S^{OH} = \Delta C_{OH} / \Delta C_{Ce}$ and $n_S^{Cl} = \Delta C_{Cl} / \Delta C_{Ce}$. When $k = 2.5$ $n_S^{OH} = x/m = 5/2 = 2.5$ and $n_S^{Cl} = y/m \cong 1/2 = 0.5$, which corresponds to the basic salt $Ce(OH)_2Cl$. As observed within the range k $1.25 \div 2.75$ the results of the calculations practically coincide with the measured values of the residual concentrations of ions in the precipitate. Some deviations of the C_{Cl}^r calculated values from the experimental ones when $k > 2.75$ are due to the neglect of the Ce^{3+} hydrolysis process in the basic medium [19].

Table 4. Results of analysis and calculation of residual concentrations in the system „$CeCl_3 - NaOH - H_2O$". $C_{Ce}^0 = 0.025M$, $C_{Cl}^0 = 0.075M$, $t = 25^0C$

k	Analysis and calculation* [16]			Our calculation	
	pH	$C_{Ce}^r \cdot 10^2, M$	$\Delta C_{Ce}^* \cdot 10^2, M$	$C_{Ce}^* \cdot 10^2, M$	$C_{Ce}^r \cdot 10^2, M$
0.25	5	2.29	0.21	0.625	2.29
0.5	5	2.08	0.42	1.25	2.08
0.75	5	1.92	0.63	1.875	1.87
1.0	5	1.65	0.85	2.5	1.65
1.25	5	1.41	1.09	3.125	1.41
1.5	6	1.07	1.43	3.75	1.07
1.75	7	0.85	1.65	375	0.84
2.0	75	0.58	1.92	5.0	0.58
2.25	8	0.26	2.24	5.625	0.25

Table 5. The results of the analysis and calculation of the residual chloride ion concentration in the „$CeCl_3 - NaOH - H_2O$" system. $C_{Ce}^0 = 0.025M$, $C_{Cl}^0 = 0.075M$, $t = 25^0C$

k	Analysis and calculation* [18]			Our calculation	
	pH	$C_{Cl}^r \cdot 10^2, M$	$\Delta C_{Cl}^* \cdot 10^2, M$	$\Delta C_{OH}^* \cdot 10^2, M$	$C_{Cl}^r \cdot 10^2, M$
1.25	5	7.4	0.1	3.125	7.40
1.5	6	7.2	0.3	3.75	7.20
1.75	7	7.01	0.49	375	7.01
2.0	75	6.9	0.6	5.0	6.90
2.25	8	6.65	0.85	5.625	6.65
2.5	5.3	6.45	1.05	6.25	6.45
2.75	6.8	7.02	0.48	6.83	7.02
3.0	11.0	7.21	0.29	7.12	7.19
3.5	11.3	7.29	0.21	7.3	7.25
0	11.4	7.37	0.13	7.4	7.33

CONCLUSION

It should be noted that the proposed method of calculating K_S has a number of advantages compared to those traditionally used. The proposed method of calculating K_S has a number of advantages compared to those traditionally used. First, instead of the residual concentrations of the salt components, only the pH value of the saturated solution was used in the deduced equations. Thus, the number of independent variables, which need to be determined experimentally, was reduced. At the same time, the potentiometric method used to determine the pH, was sufficiently accurate, simple and universal and does not require the use of ion-selective electrodes. At the same time, C_i^r was usually determined by chemical methods, which cede in most cases, for several reasons, compared to the potentiometric method. Second, the K_S value calculated here has a thermodynamic character. This is obtained not by extrapolation to the ionic force equal to zero, but on the basis of thermodynamic constants and $pH = -\log a_{H^+}$.

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