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PHYSICAL CHEMISTRY

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Abstract

Full Text

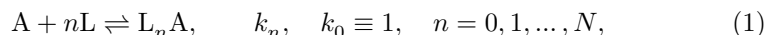
PHYSICAL CHEMISTRY

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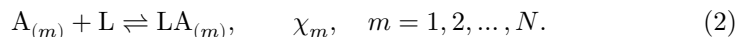
SOME PROPERTIES OF THE FORMATION FUNCTION AND RELATED QUANTITIES

(Presented by Academician A. A. Grinberg on 16 IX 1964)

In theoretical studies it is important and useful to compare the properties of a system with multistep equilibrium



and of a system with N single-step equilibria



It is no less important to try to reduce calculations of the additive properties of system (1) to calculations of system (2), since special tables have been compiled for manual calculation in systems (2) ^(1,2), and in machine calculation the compilation of universal programs is facilitated.

If G is an additive property of the entire group of substances formed with the participation of A , and g_n is the partial property of $L_n A$, then for system (1)

$$G = \sum_{n=0}^N g_n [L_n A] = \sum_{n=0}^N g_n k_n \varphi_n a l^n, \quad (3)$$

where $[L_n A]$ is the equilibrium concentration of $L_n A$; a is the activity of A ; φ_n is the reciprocal of the activity coefficient of $L_n A$. It is useful to introduce the average value of property (3)

$$\bar{g} = G/c = \frac{\sum_{n=0}^N g_n k_n \varphi_n l^n}{\sum_{n=0}^N k_n \varphi_n l^n}, \quad (4)$$

where $c = \sum [L_n A]$ is the analytical concentration of A , a quantity of type (3) in the case $g_n \equiv 1$.

Formula (4) can determine various properties calculated per 1 mole of substance A : the number of moles of bound ligands L , or the formation function \bar{n} when

$g_n = n$; the contribution to the optical density if g_n are the coefficients of molar absorption; the doubled contribution to the ionic strength if $g_n = (a + n\lambda)^2$, where a and λ are the charges of particles A and L, etc.

The desired transformation, relating systems (1) and (2), is the decomposition of the fractional rational function (4) of the variable l into simple fractions (4):

$$\bar{g} = g_N + \sum_{m=1}^N g_m (1 + \chi_m \xi_m l)^{-1}. \quad (5)$$

Each term of (5) is the average value (4) of equilibrium (2) with constant χ_m and activity correction $\xi_m = \varphi_{1(m)}/\varphi_{0(m)}$.

On the basis of theorems of higher algebra (4), using substitutions and transformations, one can obtain formulas for calculating the parameters of expansion (5). $\chi_m \xi_m$ are roots of the equation

$$\varphi_0(\chi\xi)^N - k_1\varphi_1(\chi\xi)^{N-1} + k_2\varphi_2(\chi\xi)^{N-2} - \dots + (-1)^N k_N\varphi_N = 0, \quad (6)$$

and expansion (5) is possible if all roots of (6) are real. The constants

x_m are roots of (6), if all activity corrections $\xi_m = \varphi_n = 1$. The properties of the corresponding system of one-stage equilibria (2) are calculated by the formula

$$g_m = - \sum_{n=0}^N g_n (-1)^n k_n \varphi_n (x_m \xi_m)^{N-m} / \sum_{n=0}^N n (-1)^n k_n \varphi_n (x_m \xi_m)^{N-m} = \sum_{n=0}^N g_n d_{mn}, \quad (7)$$

where d_{mn} is the value of g_m for the fraction of the n -th particle in system (1) (its degree of formation (5))—a property (3) for which $g_n = \delta_{in}^*$,

$$d_{mn} = - \sum_{i=0}^N \delta_{in} (-1)^i k_i \varphi_i (x_m \xi_m)^{N-i} / \sum_{i=0}^N i (-1)^i k_i \varphi_i (x_m \xi_m)^{N-i}. \quad (8)$$

To calculate the constants x_m , the quantities related to them, and the coefficients d_{mn} , it is convenient to use series in small parameters—the constants of the disproportionation equilibria:



Then the constants x_m are expressed as a product of stepwise formation constants, i.e., the equilibrium constants

$$L_{m-1}A + L \rightleftharpoons L_m A, \quad K_m = k_m k_{m-1}^{-1}, \quad (10)$$

multiplied by correction factors—series in R_m , the first terms of which are found from equation (6) by the method of undetermined coefficients (6):

$$x_m = K_m [1 + (R_{m-1} - R_m) + (R_{m-1} - R_m)(2R_{m-1} + R_m) - R_{m-2}R_{m-1}^2 + (R_{m-1} - R_m)(5R_{m-1}^2 + 2R_{m-1}R_m + 2R_m^2) + R_m^2 R_{m+1} + \dots], \quad (11)$$

$$\lg x_m = \lg K_m + \lg e \cdot \{(R_{m-1} - R_m)[1 + \frac{3}{2}(R_{m-1} + R_m) + \frac{1}{3}(10R_{m-1}^2 + 7R_{m-1}R_m + 10R_m^2)] - R_{m-2}R_{m-1}^2 + R_m^2 R_{m+1} + \dots\}. \quad (12)$$

Here and below it is assumed that $R_m = 0$ for $m \geq N$ and $m \leq 0$.

Substitution of (11) into (8), with the corresponding transformations, gives, without taking activity corrections into account, the following series in R_m , convenient for calculating d_{mn}^{**} and, from them by (7), g_m :

$$d_{m,m-3} = R_{m-2}R_{m-1}^2 + \dots,$$

$$d_{m,m-2} = -R_{m-1}(1 + 3R_{m-1} + 10R_{m-1}^2 - 2R_{m-1}R_m + R_m^2) + \dots,$$

$$d_{m,m-1} = 1 + 2R_{m-1} + R_m + 6R_{m-1}^2 + 3R_m^2 - 3R_{m-2}R_{m-1}^2 + 20R_{m-1}^3 - 3R_{m-1}^2 R_m + 10R_m^3 - 2R_m^2 R_{m+1} + \dots, \quad (13)$$

$$d_{m,m} = -(1 + R_{m-1} + 2R_m + 3R_{m-1}^2 + 6R_m^2 - 2R_{m-2}R_{m-1}^2 + 10R_{m-1}^3 - 3R_{m-1}R_m^2 + 20R_m^3 + 3R_m^2 R_{m+1}) + \dots,$$

$$d_{m,m+1} = R_m(1 + 3R_m + R_{m-1}^2 - 2R_{m-1}R_m + 10R_m^2) + \dots,$$

$$d_{m,m+2} = R_m^2 R_{m+1} + \dots$$

We have not succeeded in investigating the region of convergence of the series (11)–(13); however, in applying them to calculations and from heuristic considerations, one may assume that they converge for not too large R_m (i.e.,

* δ_{in} is the Kronecker symbol; $\delta_{in} = 1$ for $i = n$; $\delta_{in} = 0$ for $i \neq n$.

** For $n > m + 2$ and $n < m - 3$, the series d_{mn} begin with terms higher than the third degree in the small parameters R_m .

for formation step constants that are not too close), when (6) gives real distinct roots.

Application of formula (7) to the formation function $g_n = n$ gives, independently of activity corrections, $\vartheta_m = -1$ for all m . Expansion of the formation function into partial fractions was earlier used by Simms (7) to calculate acid-base equilibrium constants from titration curves.

Application of the derived formulas to the mean square of the charge gives:

$$\overline{(\alpha + n\lambda)^2} = (\alpha + N\lambda)^2 - \sum_{m=1}^N (2z_m + \lambda)\lambda(1 + \nu_m \xi_m l)^{-1}, \quad (14)$$

where z_m , the “charge” (nonintegral) of the particle $A_{(m)}$, is determined by the series

$$z_m = \alpha + (m - 1)\lambda + \lambda[(R_{m-1} - R_m)(1 + 3R_{m-1} + 3R_m + 10R_{m-1}^2 + 7R_{m-1}R_m + 10R_m^2) - 3R_{m-2}R_{m-1}^2 + 3R_m^2R_{m+1} + \dots]. \quad (15)$$

If, as in the Debye-Hückel theory (neglecting differences in the ionic-size parameter), one assumes

$$\varphi_n = \varphi^{(\alpha+n\lambda)^2}, \quad (16)$$

where φ is the reciprocal of the activity coefficient of a singly charged particle, the first term of the Taylor expansion of $\lg \xi_m$ in $\lg \varphi$, obtained with the aid of (6), gives the computational formula

$$\lg \xi_m \simeq (2z_m + \lambda)\lambda \lg \varphi, \quad (17)$$

where z_m is the same as in (14). The accuracy of (17) depends on $\lg \varphi$, i.e., on the ionic strength, and to estimate the accuracy one may use the following term of the Taylor series, in which the multiplier of $(\lg \varphi)^2$ is expressed by the series

$$2\lambda^4 \ln 10 [(R_{m-1} - R_m)(1 + 6R_{m-1} + 6R_m + 30R_{m-1}^2 + 21R_{m-1}R_m +$$

$$\begin{aligned}
 &+ 30R_m^2 + 140R_{m-1}^3 + 70R_{m-1}^2 R_m + 70R_{m-1} R_m^2 + 140R_m^3) - \\
 &- 64R_{m-2} R_{m-1}^3 + 16R_{m-2} R_{m-1}^2 R_m - 16R_{m-1} R_m^2 R_{m+1} + 64R_m^3 R_{m+1} + \dots]. \quad (18)
 \end{aligned}$$

The expansion into partial fractions has been successfully applied to the calculation of the curve of acid-base titration with allowance for the influence of ionic strength ⁽¹⁾, and may find other important and varied applications.

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Note: Figure translations are in progress. See original paper for figures.

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