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Abstract

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INVESTIGATION OF CERTAIN FUNCTIONS CHARACTERIZING THE STATE OF A SUBSTANCE IN SOLUTION

The question of the regularities in the change of the state of a substance in solution upon a quantitative change in the composition of the solution is of substantial interest for chemical theory and practice. In the present communication we have in mind solutions in which the dissolved substances A and B may occur both in the free state and in the form of a series of compounds $A_{m_i}B_{n_i}$, having one or another equilibrium concentration y_i. The dependence of the state of a substance in such systems on its own concentration or on the concentration of another substance can be represented mathematically with the aid of various functions, which are defined by the system of equations

$$y_i = K_i a^{m_i} b^{n_i}, \tag{1}$$

expressing the application of the law of mass action to each of the equilibria

$$m_i A + n_i B \rightleftarrows A_{m_i} B_{n_i} \tag{2}$$

in combination with two equations:

$$a = C_A - \sum_i m_i y_i, \qquad b = C_B - \sum_i n_i y_i, \tag{3}$$

which express the relation between the equilibrium concentrations a and b of the reacting substances and their initial concentrations C_A and C_B. The condition for constancy of the values K_i upon a quantitative change in the composition of the solution is the constancy of the activity coefficients of all forms participating in the equilibrium. Negative values that may be assigned to m_i or n_i in the case where equation (2) corresponds to the formation of hydrolysis products with elimination of an H^+ ion are not considered in the present communication, although the general approach to the study of such reactions is the same as for positive m_i and n_i ([1]). The change of each function is considered by us at constant total concentration of component A and variable concentration of component B. No properties characterizing its nature (metal cation, anion, neutral molecule, etc.) or the place occupied in the structure of the compound (central group, addend) are thereby assigned to either of the components; this ensures the applicability of all the conclusions to cases of changing the concentration of any substance participating in the formation of compounds.

The general character of the change in each function studied by us can be represented as a result of analyzing it for a maximum and a minimum in the region of finite concentrations of B and determining its limiting values in the region of sufficiently large and in the region of sufficiently small concentrations of the given component (the region of microconcentrations is of special interest for radiochemistry ([2])).

In the present communication only the principal results of the mathematical analysis carried out are presented.

Let us first consider the region of finite concentrations of component B. The function y, characterizing the change in the concentration of some compound $A_{mB}n$ (chosen arbitrarily from the series $A_{m_i}B_{n_i}$), passes

passes through a maximum at the point whose position satisfies the equality

$$\sum_i (n_i m - n m_i) m_i y_i = na. \tag{4}$$

As further analysis shows, a necessary and sufficient condition for a maximum of y is a positive value of at least one of the differences $n_i/m_i - n/m$. Thus, the equilibrium concentrations of all compounds pass through a maximum, with the exception of those compounds that contain the greatest amount of B in the system relative to A: $(n_i/m_i)_{\max}$.

The function y_1/y_2, characterizing the ratio of the concentrations of some compounds $A_{m_1}B_{n_1}$ and $A_{m_2}B_{n_2}$, passes through an extremum when

$$\sum_i [n_i(m_1 - m_2) - m_i(n_1 - n_2)] m_i y_i = (n_1 - n_2) a^*. \tag{5}$$

Investigation of (5) shows that y_1/y_2 has an extremum in the case where at least one of the differences $(m_1 - m_2)/(n_1 - n_2) - m_i/n_i$ is positive; for this, in turn, it is necessary that the differences $m_1 - m_2$ and $n_1 - n_2$ have the same sign. Investigation of the second derivative of the function y_1/y_2 at the extremum point shows that, for a positive value of the last two differences, the extremum is a maximum, while for a negative value it is a minimum. If, in one or another system, all the values m_i and n_i are connected by some linear dependence, for example $m_i = tn_i + r$ (3) (t and r are constants), then the extremum of each of the ratios of the concentrations of two compounds is attained, as follows from

(5), at $a/(C_A - a) = -r$ (if $r = -1$, then $a = C_A/2$); for $r > 0$, y_1/y_2 has no extremum in the region of positive values.

The ratio y/a of the concentration of some compound $A_{mB}n$ to the equilibrium concentration of component A has a maximum when

$$\sum_i [n_i(m-1) - nm_i]m_i y_i = na. \tag{6}$$

A necessary and sufficient condition for a maximum of y/a is $n/(m-1) < (n_i/m_i)_{\max}$.

The ratio y/b reaches a maximum when

$$\sum_i [n_i m - (n-1)m_i]m_i y_i = (n-1)a. \tag{7}$$

If each m_i is equal to 1, then, in accordance with (7) and (3), we obtain $(C_B - b)/C_A = n - 1$ ($(C_B - b)/C_A$ is the mean number $\bar{n}$ of B particles in the compounds AB_{n_i} that are formed). The function y/b has no maximum (it decreases monotonically from the value KC_A^m at $C_B = 0$ to 0 at $C_B = \infty$) in the case where $n = 1$.

The product ab, close to 0 at small C_B $\left(\lim_{C_B \to 0} ab = C_A \cdot 0 = 0\right)$, with increasing C_B passes through a maximum at the point whose position satisfies the equality

$$\sum_i (n_i - m_i)m_i y_i = a, \tag{8}$$

for whose fulfillment it is necessary and sufficient that the content of B exceed the content of A in at least one of the compounds. If all m_i are equal to 1, then, in accordance with (8) and (3), $(C_B - b)/C_A = 1$ ($\bar{n} = 1$).

* Summation in all cases is carried out over the values of i corresponding to each of the compounds $A_{m_i}B_{n_i}$ (

The conditions for a maximum of the products y_1y_2, ya, and yb can be obtained, respectively, from equalities (5), (6), and (7) by replacing the minus sign by a plus sign in each of the parentheses in these equalities.

The quantities a on the right-hand side of each of equalities (4)–(8) can be replaced by C_A; for this, in accordance with (3), it is sufficient to replace m_i (but not m, m_1, and m_2) inside the parentheses on the left-hand side of these equalities by $m_i - 1$.

The function y/C_B, which characterizes the fraction of the compound $A_{mB}n$ relative to the total concentration of component B, may have one or more than one extremal point—in accordance with the condition

$$\left(mC_B - \sum_i m_i n_i y_i\right) \sum_i m_i n_i y_i =$$
$$= \left[(n-1)C_B - \sum_i (n_i - 1) n_i y_i\right] \left[C_A + \sum_i (m_i - 1) m_i y_i\right]. \qquad (9)$$

If all m_i and n_i are connected by a linear dependence $m_i = t(n_i - 1)$ (the special case of the dependence $m_i = tn_i + r$ when $r = -t$), then y/C_B, in the case of the compound with the highest content of A and B in the system, has a single maximum at $a/(C_A - a) = t$; for the remaining compounds y/C_B has a minimum at $a/(C_A - a) = t$ and two maxima, whose positions satisfy the equality $\sum_i (n_i - 1) n_i y_i = (n-1)C_B$. If each n_i is equal to 1, then y/C_B has a single maximum at $\bar{m} = (C_A - a)/C_B = m$ ($\bar{m}$ is the average number of A particles in the compounds $A_{m_i}B$). In the case $a = C_A = \text{const}$, y/C_B has one maximum, whose position satisfies the equality $\sum_i (n_i - 1) n_i y_i = (n-1)C_B$. The latter expression does not contain m_i, since the quantities a^{m_i} in equations (1), when $a = \text{const}$, enter into the values of the equilibrium constants. Constancy of a occurs in the case $C_B \ll C_A$, and also in hydrolysis in buffer solutions (the sign of the quantities m_i is negative if a is understood as $[H^+]$; in the present case this plays no role).

The presence of extrema is also characteristic of various functions reflecting the overall result of the interaction of A and B in the system; among them (for $C_A = \text{const}$) are: C_B/b, $(C_A - a)/\sum_i y_i$, $(C_B - b)/\sum_i y_i$, $(C_A - a)/C_B$, $(C_B - b)/(C_A - a)$, $a + \sum_i y_i$, $(b + \sum_i y_i)/C_B$, $(a + b + \sum_i y_i)/(C_A + C_B)$, and others; some of these functions are used in calculating constants of compound formation ([1]). As an example, we give the relations obtained by us for the extremal points of the functions C_B/b and $(C_B - b)/(C_A - a)$:

$$\left(\sum_i m_i n_i y_i\right)^2 = \sum_i (n_i - 1) n_i y_i \left[C_A + \sum_i (m_i - 1) m_i y_i\right], \qquad (10)$$

$$\left[\sum_{i_k \neq i_l} (m_{i_k} n_{i_l} - m_{i_l} n_{i_k})^2 y_{i_k} y_{i_l}\right] \Big/ \left[\sum_{i_k \neq i_l} (n_{i_k} - n_{i_l})(m_{i_k} n_{i_l} - m_{i_l} n_{i_k}) y_{i_k} y_{i_l}\right] =$$
$$= a/(C_A - a), \qquad (11)$$

where $\sum_{i_k \neq i_l}$ denotes summation over all pairwise combinations of the values y_i and the corresponding pairwise combinations of the values m_i, as well as n_i. If each n_i is equal to 1, then C_B/b, as is evident from (10), has no extremum; if each n_i is equal to $t(m_i-1)$, then C_B/b passes through a maximum at $a/(C_A-a)=t$. The ratio $(C_B-b)/(C_A-a)$, which characterizes the average composition of the compounds $\bar{n}/\bar{m}$ in the case $m_i = tn_i + r$, has, as follows from (11), an extremum (minimum) at $a/(C_A-a) = -r$.

All the results presented above pertain to the study of the region of finite concentrations of B. Consideration of the region of sufficiently large concentrations leads to the conclusion that, as $C_B \to \infty$, in the limit all forms are expressed, except those for which $n_i/m_i = (n_i/m_i)_{\max}$. The limiting ratio of the concentrations of any two compounds $A_{m_1}B_{n_1}$ and $A_{m_2}B_{n_2}$, for which $n_1/m_1 < (n_i/m_i)_{\max}$ and $n_2/m_2 < (n_i/m_i)_{\max}$, is the indeterminacy 0/0; resolving it shows that $\lim_{C_B\to\infty}(y_1/y_2)$ for the given pair of compounds is either 0, if $n_1-n_2 < (m_1-m_2)(n_i/m_i)_{\max}$, or ∞, if $n_1-n_2 > (m_1-m_2)(n_i/m_i)_{\max}$, or a finite quantity if $(n_1-n_2)/(m_1-m_2) = (n_i/m_i)_{\max}$. In the special case where $n_1/m_1 = n_2/m_2 < (n_i/m_i)_{\max}$, $\lim_{C_B\to\infty}(y_1/y_2)$ is 0 if $m_1 > m_2,\ n_1 > n_2$, and ∞ if $m_1 < m_2,\ n_1 < n_2$.

When considering the region of microconcentrations, it is essential to study $\lim_{C_B\to 0}(y/C_B)$ and $\lim_{C_B\to 0}(y_1/y_2)$. The first of these limits is equal to 0 if $n > 1$, and to a finite quantity if $n = 1$; the second is equal to 0 in the case $n_1 > n_2$, to ∞ in the case $n_1 < n_2$, and to $(K_1/K_2)C_A^{m_1-m_2}$ in the case $n_1 = n_2$. Thus, in the region of very small C_B, in contrast to the region of very large C_B, the principal tendency in the change of the state of the substance is determined not by the ratio of B and A in the compounds formed, (n_i/m_i), but by the absolute content of B in them, (n_i). This tendency is consistent with the general limiting law of chemical interaction at microconcentrations, which, as the corresponding analysis based on the general form of the stoichiometric equation shows, is as follows: at an infinitely small concentration of one or several components, the reaction proceeds irreversibly in the direction of increasing the total number of moles of the microcomponents. Transfer of component B from the left-hand side of stoichiometric equation (2) to the right-hand side leads, for $n_i > 1$, to a decrease in the number of moles of this component, and consequently, in the case where B is the microcomponent, all compounds containing more than one particle of B dissociate completely in the limit ($\lim_{C_B\to 0}(y/C_B) = 0$).

The presence of extrema in such functions as y/C_B and C_B/b shows, however, that the transition to this limiting state of complete dissociation of the microcomponent is not monotonic; in one or another interval of concentrations of B, both the fraction of individual compounds $A_{m_i}B_{n_i}$ and the overall completeness of binding of this component (C_B/b) may increase as its concentration decreases.

Thus, the study carried out of a number of functions that include the values of the equilibrium concentrations of the forms produced by the substance in the systems under consideration makes it possible to note certain regularities in the change of the state of the substance in these systems over the entire concentration range.

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