**DETERMINATION OF ENTHALPIES OF COMPLEX FORMATION REACTIONS FROM TEMPERATURE COEFFICIENTS OF THE METAL ION EQUILIBRIUM CONCENTRATION**

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The reactions of complex formation of an arbitrary composition  in aqueous solutions are represented here by the following scheme:

  (1)

Near the reaction equation the related thermodynamic characteristics are written, namely, the equilibrium constant  and the enthalpy of the complex formation reaction  at the temperature *T* (below this index is omitted).

 There are generally two experimental methods for determining the enthalpies: *a*) direct calorimetric measurements of the variation of the total caloric effect of reactions and *b*) the  calculation from the temperature dependences  or variation of the Gibbs energy  of the reactions for different temperatures.

The most general and accurate method is the calorimetric determination of , but this method in a number of cases, especially for elevated temperatures, involves high technical difficulties [1].

Within the second method the  calculation is performed according to the equation of reaction-isobar or Gibbs-Helmholtz equation:

 (2)

 (3)

Therefore, for the  determination it is necessary to know the dependency on temperature of the equilibrium constant or Gibbs energy change.

 The equations, which determined the dependence of temperature coefficients of the degree of complexation  on the variation of enthalpies of complex formation reactions, were derived in [2, 3]. In this context, it is of interest to estimate the possibility of determining  ​​from the  values and equilibrium constants at one temperature *T*.

 Authors [3] deduced the equation that takes into account the relationship between the temperature coefficient  and the sum of variations of enthalpies  of separate reactions:

 (4)

where  are the weighting coefficients, determined by the relationship:

 (5)

Here  and  symbolize the total concentrations of ligand and metal ion in solution, and  denotes the molar fraction of the  complex:

 (6)

The functions  and , for a number of real systems, were examined in [4]. In the case of stepwise reactions in solution () the equations (4) and (5) simplify and take the form [3, 4]:

 (7)

 (8)

Weighting coefficients are calculated using the equations (5) and (6) for certain values  ​​and . The temperature coefficients  are determined by differentiating the tabulated experimental data  or through differentiating by temperature the equation of temperature dependence .

For a number of real systems the best approximation equation of the dependence  is found to be:

 (9)

where *A – E* are the constants for values  and , obtained by computerized treatment of data by the method of least squares. By differentiating the equation (9) in respect to *T,* the requested value of the temperature coefficient  is obtained. One can state that for  :

, (10)

where  is the equilibrium concentration,  and  symbolize the activity and activity coefficient of the metal ion, respectively.

 The processing of experimental data can be practically carried out by numerical methods, if for data  and  there are not less than five experimental values ​​ (or ) for different temperatures [5, 6]. Also, for convenience, it is necessary to keep constant the area of the temperature variation (, where is the step of differentiation). Consequently, in the case of formation of *N* complexes for determining *N* values of the variation of reaction enthalpies  (1) it is necessary to solve a system of *N* linear equations, written on the basis of the equation (4) and the respective *N* values ​​ of , while maintaining invariant the total concentration of the metal ion .

 If under certain parameter values  and  just a single complex is formed in observable quantity, then equation (7) takes the form:

 (11)

Comparing equations (2) and (11) one can conclude that if the accuracy of the  and (or ln[M]) measurements is similar, then the error of the determined values ​​is a quantity of the same order. Equation (11) allows the approximate estimation of the actual error of the  determination. Thus, the error in the  0.5 kJ/mol in the range of 300 K and the temperature variation interval of 10 degree corresponds to the or value variation of 0.007 log units.

**References**

1. А.М. Panfilov, N.S. Semionova. *Calculation of the thermodynamic properties at high temperatures.* Educational electronic text edition, Moscow, 2009. (Rus.)
2. I. Fishtik, I. Povar. *Zh. Neorg. Khim*. **35** (1990) 102.
3. I. Fishtik, I. Povar. *Zh. Neorg. Khim*. **35** (1990) 108.
4. I. Povar. *Zh. Neorg. Khim*. **38** (1993) 1902.
5. J. Forsyte, M. Malkolm, K. Mouler. *Machine Methods of Mathematical Calculations.* Mir (World), Moscow, 1980.
6. E. A. Bender. *An introduction to mathematical modeling*. Dover Publications, N.Y., 2000.