

## **THERMOANALYTICAL APPROACH TO THE STUDY OF THE KINETIC AND THERMODYNAMIC STABILITY OF COORDINATION COMPOUNDS AND CLATHRATES**

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The possibilities of the modern thermoanalytical methods for the study of the kinetic lability and thermodynamic stability of coordination compounds and inclusion compounds are discussed. The nonisothermal kinetics allowed to obtain the kinetic stability series of compounds (iso-entropy, iso-enthalpy and with iso-kinetic temperature), these series are considered from the point of view of the ligands substitution mechanism. The quasi-equilibrium thermogravimetry was used for the forming of thermodynamic stability series and for the search of the iso-equilibrium temperature.

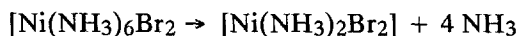
The coordination chemistry investigates the compounds, in which the ligands form the coordination sphere around the central atom. The material on the complex structure was collected, in general, by the crystal substances investigations, but the present-day knowledge of ligands substitution processes, of the complex formation mechanism, of the substances kinetic stability, of their reactivity are based on the study of the reactions in the solutions. On this basis the coordination chemistry can be called the chemistry of dissolved coordination compounds, and in the book "Mechanisms of Inorganic Reactions" by Basolo and Pearson only one page from 500 pages is dedicated to the solid state reactions [1].

The energy of extra-stabilization in the complexes of *d*-elements, thermodynamic and kinetic aspects of the trans-influence statistical effect in the mutual influence of the ligands, - all this meaningful subject-matter of the coordination chemistry paradigm, was created by investigations of the reactions in solutions.

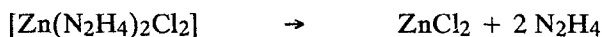
The reactions, which take place in solid coordination compounds, are studied in far lesser degree, and the regularities, observed in these reactions, enter into the scientific basis of coordination chemistry in very small degree.

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We shall discuss here thermal dissociation processes of the complex compounds with the removal of volatile ligands and with the formation either of the next complex (with lesser number of ligands) or of simple non-complex salt:



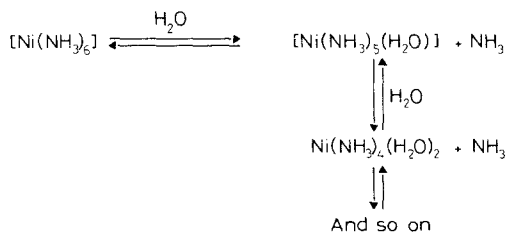
The essential feature of these processes of ligands substitution (because of the solvation absence) is the understandable decrease of the number of ligands in the inner sphere, and this results in diminishing of the coordination number of the central atom. The remaining ligands increase their density, become the bridging ones.



octahedron with bridging hydrazine ligands

tetrahedron with bridging chlorine ions

If we shall discuss the processes in the solution, the solvation always changes over any transformation of the coordination sphere into the ligands substitution process with the possible conservation of the coordination number, and the coordination of solvent molecules makes possible to realize in the solution a big number of partially substituted forms ("stepping equilibrium"):



The topochemical control over the solid state reactions, and also thermodynamic and kinetic restrictions lead to very small number of the intermediate phases in the intricate reaction of the thermal decomposition of the

initial high-ligands complex compound to the final product: to the simple salt (or to the complex with non-volatile ligands).

## Experimental

The thermal dissociation processes of complex compounds are studied last two decades very actively. The situation occurred that the main groups of investigators formed from the chemists, working with coordination compounds synthesis, and acquired the knowledge of the thermoanalytical methods for the investigation of these reactions. The advance and propagation of the non-isothermal kinetics arose in appreciable extent from the demands of these works for the quantitative investigation of the reactivity in the thermal decomposition reactions within big series of compounds.

The understandable requirements to the experiments were formulated: the heating rate within limits from 2 to 10 deg/min, the sample mass is in limits of several milligrams, the fraction  $f$  of grains with minimum size distribution ( $d_{\max}/d_{\min} \leq 5$ ), the sufficient shift from the equilibrium state (the inert gas flow through the sample), the absence of temperature and concentration gradients inside the sample volume.

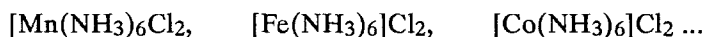
We used gas-flowing reactor for non-isothermal kinetic experiments ( $W_{\text{He}} = 60\text{-}100 \text{ cm}^3/\text{min}$ , conductometric detector for recording of gas-evolution curves). The integral method and the computer programme by Šesták and Škvara were used for the kinetic analysis of the experiments [2]. In this method the selection of the kinetic equation is carried out by linearity of the function  $\lg g(\alpha)$  vs.  $1/T$ . The search is made amongst 13 equations, valid for nucleation, nuclei growth, diffusion, reaction on the interface. In all cases the rate-controlling process was the chemical reaction on the interface: equation of the contracted sphere.

We used quasi-equilibrium thermogravimetry (Q-derivatograph) - specific thermoanalytical method, based on the maintenance of the small and constant decomposition rate (0.16 mg/min). Working with special set of sample holders with different hindrance of gas evolving (plate-like holder, open crucible, crucible with a lid, labyrinth holder) allows to run the experiment in quasi-isobaric conditions ( $p_{\text{gas}} = 0.01, 0.05, 0.2, 1.0 \text{ atm}$ ). The decomposition temperature for the reactions with easy reversibility stabilizes till almost the end of the every reaction step. These temperatures are close to equilibrium temperatures ( $A_s \rightleftharpoons B_s + C_{\text{gas}}$ ) at definite pressure of  $C_{\text{gas}}$ . These temperatures can be used for the formation of the row of ther-

modynamic stability of compounds. It seems that the sharp stabilization of the temperature (the formal order of the reaction is equal to zero) in some cases is connected with the formation and moving of the thin decomposing layer throughout the sample volume in accordance with the small temperature and pressure gradients.

## Results and discussion

In the coordination chemistry the change of the properties in the series of substances traditionally has a great significance. This change in characteristics is very important for the interpretation of peculiarities of the structure and reactivity (for example, substitution processes). Such series of compounds is formed by the change of the central atom:



or by the change of the innersphere ligand, or by the change of the outersphere ion.

For the kinetics the comparison of the rate constants only is not quite enough, so as they apply to one temperature, which is chosen as desired. It is more interesting to examine separately the enthalpy and entropy contributions to the kinetic stability along the series of compounds.

### *Complexes of transition metals with aniline derivatives*

We investigated the decomposition of transition metals complexes with methylaniline and toluidines. If we compare the stability by the rate constants value or by the initial temperature of decomposition, for all these series we have normal row of stability: the nickel complex is the most stable. For all toluidines complexes both the row of rate constants and activation energies are normal; the preexponential factor is the same through the row all kinetic stability is determined by the activation energy only. For methylaniline complexes the increase of kinetic stability in row contradicts with the behaviour of activation energy. Greatest activation energy value has the manganese complex, the least - the nickel complex. In this row the increase of stability is determined by preexponential factor (Fig. 1). We can suggest, that for toluidine complexes the rate-controlling step is the breaking of the metal-ligand bonds. For methylaniline complexes the rate-control-

ling step appears to be the formation of new bonds, the initial sphere transforms into the polyhedron with bridging chlorine ions.

This is alike the dissociation and the association mechanisms in the ligands substitution in solutions ( $S_{N1}$  and  $S_{N2}$ ).

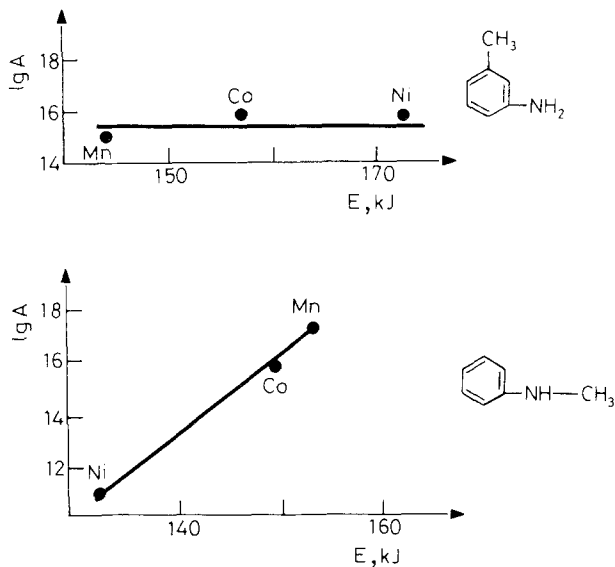


Fig. 1 Kinetic parameters of the thermal decomposition for  $[MA_2Cl_2]$  - complexes ( $A = m$  - toluidine, methylaniline)

#### *Dehydration of aqua-acidocomplexes with aminoacids*

We studied the dehydration of two series of chelates of ethylenedinitrilotetraacetic acid (EDTA). The chelates are binuclear; the structures of complexes are different. All manganese complexes are isostructural:  $[Mn(H_2O)_4O_1O_{II}][ML] \cdot 2H_2O$ . All calcium complexes have different structures, with different number of coordinated water molecules and oxygen atoms from organic ligand in calcium coordination sphere.

It is seen on Fig. 2, that the behaviour of the kinetic stability is different in two series: in manganese row the copper complex has a maximum activation energy, in calcium row the copper complex has a minimum value of activation energy. From the energetic point of view the copper complex is the

most stable in manganese row and the most labile in the calcium row (again we can propose  $S_{N1}$  and  $S_{N2}$  mechanisms).

For the dehydration processes of  $MgNiL \cdot 6H_2O$  and  $MgCoL \cdot 6H_2O$  complexes the iso-equilibrium temperature was obtained after using full set of sample holders (Fig. 3):  $Co < Ni (> 153^\circ)$ ,  $Co > Ni (< 153^\circ)$ .

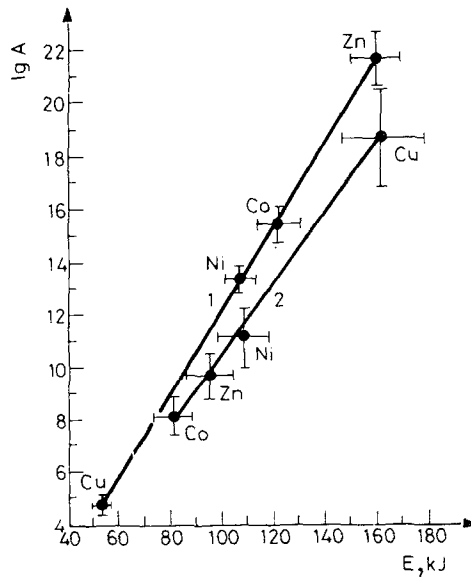


Fig. 2 Kinetic parameters of thermal dehydration for EDTA-chelates  $CaML \cdot nH_2O$  (1) and  $MnML \cdot 6H_2O$  (2), where  $M = Co, Ni, Cu, Zn$ . Error are shown at a reliability coefficient of 95%

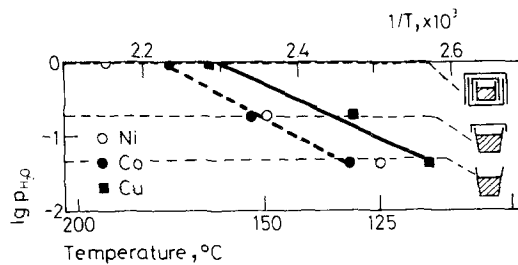


Fig. 3 Temperatures of the quasi-equilibrium dehydration of EDTA-chelates  $MgML \cdot 6H_2O$  in different sample holders: 1 - labyrinth holder, 2 - crucible with a lid, 3 - standard open crucible ( $q = 0.5 \text{ mg/min}$ )

The carbon fluoride  $C_2F_x$  ( $x \approx 1$ ) forms the inclusion compounds  $C_2F_x \cdot yA$  ( $A = C_6H_6, C_6H_5Cl, CCl_4$ , etc). It is known, that several inclusion phases exist:  $R_1$  (the first step intercalate, with two molecular layers of the included component between carbon fluoride layers),  $R_2$  (the first step intercalate, with one molecular layer of the included component between carbon fluoride layers),  $R_3$  (the second step intercalate, with one molecular layer of the included compound between two carbon fluoride layers).  $R_1$  and  $R_2$  phases are stable only under with the excess of the liquid component. The thermal decomposition takes place in one step to the  $R_3$  phase at once under linear heating. This process is step-wise under quasi-equilibrium conditions (Fig. 4). The calculation shows that the excess of the liquid organic component is removed and the decomposition  $R_1 \rightarrow R_2$  takes place simultaneously at constant temperature. The next step of the mass loss corresponds to the decomposition  $R_2 \rightarrow R_3$ .  $R_1$  phase and ( $R_2$  phase + liquid component) are not distinguishable in thermodynamic sense (on this level of accuracy).

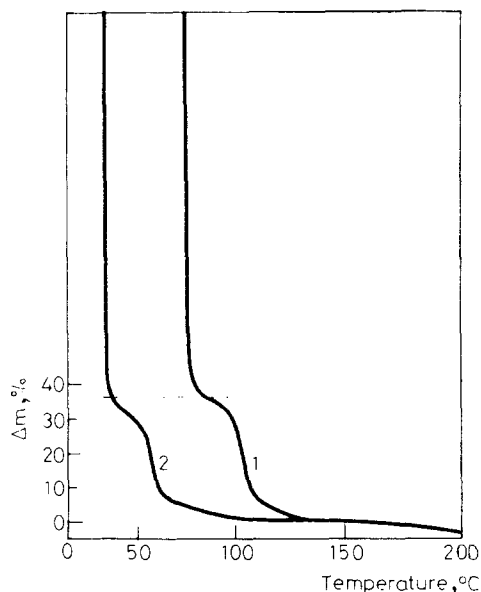


Fig. 4 Thermal decomposition of inclusion compound  $C_2F_{0.9} \cdot yCCl_4$ . Quasi-isothermal heating (0.3 mg/min); 1 - labyrinth holder, 2 - standard open crucible

Modern thermoanalytical methods allow us to obtain the quantitative information about the kinetic and thermodynamic stability in the series of compounds. This information is useful for search for the regularities in the stability of coordination compounds and inclusion compounds in the thermal dissociation processes [3-4].

## References

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- 3 V. A. Logvinenko, *Thermal Analysis of Coordination Compounds and Clathrates*. (in Russian), Nauka, Novosibirsk, 1982.
- 4 V. A. Logvinenko, F. Paulik, and J. Paulik, *Quasi-equilibrium Thermogravimetry in the Up-to-date Inorganic Chemistry* (in Russian), Nauka, Novosibirsk, 1989.

**Zusammenfassung** — Es werden die Möglichkeiten moderner thermoanalytischer Methoden für die Untersuchung der kinetischen Labilität und der thermodynamischen Stabilität von Koordinations- und Einschlußverbindungen diskutiert. Die nichtisotherme Kinetik erlaubt die Erstellung von kinetischen Stabilitätsreihenfolgen der Verbindungen (Iso-Entropie, Iso-Enthalpie und mit isokinetischer Temperatur). Diese Reihenfolgen wurden auch vom Gesichtspunkt des Mechanismus der Ligandensubstitution her bewertet. Eine quasi-Gleichgewichts-Thermogravimetrie wurde zur Erstellung der Reihenfolge der thermodynamischen Stabilität und zur Ermittlung der iso-Gleichgewichtstemperatur benutzt.