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Dedicated to Dr. Robert Mackenzie on the occasion of his 75th birthday

NATURE AND PHILOSOPHY OF THERMAL PROCESSES IN MINERALS AND INORGANIC MATERIALS

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Abstract

Solid-state thermal processes have their own specificity, distinguishing them from the processes in gases and liquids. This specificity includes, among others, their limited reversibility and the limited or modified role of chemical affinity as the main driving force indicating the direction of real solid-state processes. The consequency is the formation of metastable compounds or phases during heating, as intermediate steps towards the state of thermodynamic equilibrium. They are a results of the particular properties of the rigid internal structure of minerals and materials as the thermal reaction medium. The peculiarities of thermal reactions of solids are presented on the example of those of oxides (silicates and borates) with polymeric structures. The significance of crystal-chemical factors for the prediction or explanation of the course of high-temperature processes, as complementing the thermodynamic factors, is discussed.

Keywords: crystallization, glasses, inorganic materials, minerals, phase transformations, thermal stability, thermochemistry

Introduction

Modern methods of thermal analysis have created new possibilities for investigations of the thermal reactions of substances.

Thermal analysis has become popular as a method of determining the mineral composition of clays and other minerals specially with a low degree of crystallinity [1, 2]. Gradually, its applications have been extended to include other substances. Thermal analysis yields information on thermal reactions relatively quickly and easily. This has contributed to a rapid development of thermochemistry.

For an extension of the application of thermal methods in various fields, the monographs dealing with the thermal analysis of minerals and materials, and especially the extensive monograph edited by Mackenzie [3], were of great importance. This book is a rich source of information on the behaviour of minerals and materials during heating. It also affords a compendium of the knowledge of the high-temperature reactions occurring in these materials.

The data obtained on thermal reactions in solid bodies by means of thermoanalytical investigations [2–4], supplemented by the results of investigations of the

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structural changes accompanying these reactions, comprise a rich material which permits a search for the regularities governing these processes. This publication is an attempt at such a search.

The progress of thermal processes in solid bodies is affected considerably by their internal structure [5]. For this reason, structural thermochemistry forms a good basis for their study. An example of the advantages offered in this respect by the data on the internal structure and its transformation as a supplement to the thermodynamics of the thermal processes of solids has been given, among others, in a monograph by Mayer [6].

DSC allows measurement of the reaction enthalpy and the molar heat capacity of a substance in a wider temperature range than was possible earlier. TMA may be used to determine the isobaric coefficient of thermal volume expansion (β), the molar volume (V) and also the isothermal coefficient of compression (κ) as a function of temperature and pressure.

These are structurally sensitive thermodynamic parameters. They permit the association of thermodynamic factors with structural ones and thus lead to a better explanation of the thermal processes or a prediction of their directions.

The publication also discusses the role of crystal-chemical factors in the thermal reactions of some selected substances.

A solid body as a medium of thermal reactions

An elementary act of a chemical reaction is a result of active interactions of single atoms or ions of the reactants. For such interactions to occur, the atoms participating in them must have the necessary degree of freedom. It is known from chemical kinetics that one factor determining the reaction progress is the rate of transport of substrates to the site of reaction and the rate of removal of the reaction products.

If the chemical reactions take place not in a vacuum, but in a definite material, a gaseous, liquid or solid medium, then the atoms creating this medium, which do not participate directly in the reaction, influence the state of the reacting particles, the frequency of active collisions and the rate of displacement of the reactant atoms, and thereby affect the progress and the micromechanism of the reaction (the dilution effect), although they themselves take no part in the act of reaction.

The reaction medium may affect the degree of dispersion and the state of the reactants. This is readily observable in reactions in solutions. In some solvents, the compounds undergo electrolytic dissociation and the elements forming them pass into the state of ions. These ions may form hydration complexes (aqua ions) with the solvent molecules. Water solutions are an example here. The reactivity of the reactants is accordingly changed in this way. This is the best-known and most easily observable effect of the medium of the reaction on its progress.

In a gaseous medium, the degree of freedom of the atoms or the reactant molecules is very high and the effect of an inert gas on the state and reactivity of the reactants is usually minimal. Their behaviour is like that of a neutral solvent.

In a liquid medium, the degree of freedom of the reactant atoms is still high. The interactions between the medium particles acquire considerable importance here as the particles are close to each other.

A particular reaction medium is the surface of the condensed phases, i.e. liquids and solids. Surface chemistry supplies many examples of this.

When the reaction medium is a solid, the effect of this medium on the course of the reaction occurring in it is particularly complex. In solids, the atoms are firmly localized and they occupy definite positions in the structure. They acquire a certain degree of freedom if the ideal ordered structure of a solid becomes disturbed (defective and disordered structures). The possibilities for displacement of the reacting atoms, however, with respect to both the rate and usually the direction are limited.

The grain boundaries and the crystal defects and also dislocations and other defects of the internal structure are responsible for the fact that a solid body has the nature of a reaction medium of limited continuity.

Only those components which at the given temperature and pressure possess the appropriate reactivity may participate in solid-state reactions. To attain this, they must have sufficient freedom of displacement, which is expressed, among others, by the diffusion coefficient.

The diffusion coefficients of the various components of the given substance increase with temperature to various degrees. For this reason, some of them reach the displacement freedom earlier, which allows them to take part in the chemical reactions and to form new bonds, while others, at the same temperature, behave as a neutral matrix within which the given reaction takes place.

In many solid bodies, especially silicates and other oxide compounds, the most mobile components are the alkali metal cations and the protons. Reactions in which they participate usually begin at lower temperatures as compared with reactions involving the presence of other components.

On account of the phenomena considered above, the effect of the solid medium on the course of the chemical reactions taking place in it changes with the temperature, the pressure and occasionally also the reaction degree. The pressure and the temperature may influence the particular reactant atoms to various degrees and may cause the differentiation of their reactivity. In solids, for example, the diffusion coefficients of the atoms or ions of the particular elements change with temperature in different manners.

The influence of the medium on the course of the reactions is responsible for the fact that the operation of several general rules of chemistry and functional relationships can be modified. Accordingly, new branches of chemistry have been created; the chemistry of solutions, electrochemistry, solid-state chemistry and surface chemistry are examples.

The differences in iron cation oxidation and reduction, in the $Fe^{2+} \rightleftarrows Fe^{3+}$ equilibrium in aqueous solutions, and in the structures of solids, for example in the weathering of biotite or vermiculite, illustrate the influence of the reaction medium on the reaction course. Accordingly, functional relationships developed for reactions in vacuum or in gases require occasional correction, or their application with reference to reactions in liquids or solids is limited. An example here is the Arrhenius equation.

The factor reflecting the influence of the medium is included among others, in the values of the thermodynamic activity coefficients.

The effect of the medium may considerably modify the role of chemical affinity as a factor determining the formation of some definite compounds or the sequence of their formation in solid-state processes.

A specific feature of many solid-state medium processes is that their products are formed inside the structural framework of the parent substance (precursor) by rearrangement of the elements of this structure. They can even proceed without any visible change in the outer form of the parent crystal. Among such solid-state processes, there are some which have the character of chemical reactions and their products have chemical compositions differing from that of the parent structure. These are thermal reactions of dissociation, synthesis of new compounds, reduction and oxidation.

The term internal or intrinsic processes is proposed as a general term for processes proceeding in crystalline and also amorphous solid as their medium [7–9].

In internal reactions, each individual solid grain can be regarded as a separate thermodynamic system: closed (crystallization and recrystallization of amorphous substances, exsolution of solid solutions and phase separation of glasses) or open and exchanging matter with the gaseous or liquid surroundings (thermal dissociation, oxidation, intercalation compound formation, and metasomatic transformations of minerals). In the latter, the reaction front propagates slowly from the edges to the centre of the grain, but part of the structural framework of the parent substance is preserved and used for solid product formation.

For internal thermal dissociation, the formation of gaseous molecules and their removal outside the structural framework are often not simultaneous processes. Thermal dehydration or dehydroxylation of several hydrated borates and layer silicates are examples.

Molecules of gaseous products of dissociation are trapped within the voids in the structural framework. Their liberation occasionally induces an increase in crystal volume due to the exfoliation of the crystal along cleavage planes, or even has a sudden, explosive character. A sealed box containing vapour and burst by its pressure is a model of this process [10].

Mechanism of thermal reactions of solids

The concept of the mechanism of the thermal reactions of solids that has been used so far was based on the measurement of the kinetics of these reactions and on relating the experimental curves of the relationship between the rate and extent of reactions, $\mathrm{d}x/\mathrm{d}t=f(x)$, to functions derived from theoretical models of these processes.

The generalized rate equation is used to compute kinetic parameters for many kinds of processes. It can be expressed as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = A\exp\left(\frac{E}{RT}\right)f(x)$$

where t is time, x is the fraction reacted, T is temperature, A is the pre-exponential constant, E is the activation energy and R is the universal gas constant.

This procedure derives from the rules of the kinetics of homogeneous systems, which have been developed for reactions in the gaseous phase and subsequently extrapolated to reactions in liquids. Liquids represent continuous isotropic media, and the degree of their homogeneity is incomparably greater than that of solid bodies.

Most papers currently published in journals of thermal analysis and thermochemistry deal with the kinetics of different thermal reactions determined in this manner. However, as the number of kinetic data available on these reactions increases, the value of many of them seems to become doubtful. The question arises as to the extent to which the kinetics of homogeneous reactions can be applied to heterogeneous systems. The values of the obtained parameters E and A, the functions $f(x)$, and especially their physical meaning, are questionable.

A critical analysis of the data obtained so far leads to the conclusion that homogeneous kinetics may find application only in certain types of reactions [11–13]. In the case of reactions to which it can be applied, it is possible to select one of the theoretical equations and to determine reaction rates as a function of time and temperature. The pattern of the reaction mechanism derived on the basis of these dependences is of a very general nature. The information on the hypothetical rate limiting factor and rate equation is not sufficient to control the given process, not is it satisfactory from the scientific point of view.

The values given by different authors for the activation energy of calcite decomposition, which is the model reaction for thermal decomposition, range from 142 to 3828 kJ mol^{-1}. This can be explained as being due to the variations in the experimental conditions, and mainly the different pressures of the gaseous product of decomposition [14].

The real mechanism of decomposition determined by SEM or another experimental technique often does not correspond to the formal mechanism indicated by the kinetic function describing its rate.

The mechanism and kinetics of the internal reactions of solids are influenced by the above-mentioned intrinsic structural and morphological factors. They determine to a considerable degree the freedom of displacement of reactant atoms and the escape of gaseous product molecules. Kaolinite dehydroxylation obeys the Arrhenius kinetic equation if its plates are smaller than 1 μm [15].

However, there exist many systems for which the general kinetic equation is totally without merit, and many others (most polymer and inorganic glassy systems) for which the traditional kinetic approach is well established. This category includes the crystallization of inorganic glasses, the kinetics of which is usually well described by the Avrami-Erofeev equation. This equation is also valid for solid-melt reactions, such as those in the halogenoxy salts and MoO_3 system [16].

It should be mentioned that the exponential equations of the Arrhenius type well describe the temperature dependence of several properties of solids. The ionic electric conductivity of glasses and other inorganic substances, and the diffusion and viscosity of melts belong to this category. Their general similarities, as in the case of glass crystallization, are the elementary processes which consist in the diffusional displacement of individual ions or atoms.

For thermal reactions with such a mechanism, the Arrhenius equation may be successfully used. This is due, inter alia, to the fact that the rates of these reactions are determined mainly by the concentration and by the structural factors appropriate for the given substance, while the influence of the surroundings is less.

Even for these processes, however, the theoretical prediction does not always correspond to the experiments. The estimated directions of the growth of crystals in glass are often different from those observed under the microscope.

Traditional kinetics played a positive role at the beginning of the study of the thermochemistry of solids, but its possibilities have been virtually exhausted and any further marked progress is not to be attained in that direction.

The modified approach is expected to explain the reason and mechanism of the internal structure reconstitution processes and metastable intermediate phase formation during the heat treatment of minerals and materials. These are governed by the specific micromechanism of the rearrangement of the internal structure elements, and kinetic models based on new assumptions are necessary for them. These models must explain real processes in solid structures identified by modern instrumental methods of investigation.

Polymorphic transformations of minerals are internal structure rebuilding processes whose micromechanisms are relatively well known.

Two different mechanisms of polymorphic transformations are known: (1) diffusional displacements of individual atoms of coordination polyhedra at long distances in the crystal lattice, and (2) diffusionless transformation by the correlated rotation or displacement of atoms for short distances.

The diffusional, long-distance rearrangement of structure elements are characteristic for the slow, reconstructive polymorphic transformations connected with changes in the first coordination sphere (Al_2SiO_5 polymorphs) or for rearrangements of coordination polyhedra (SiO_4 tetrahedra displacement during the high-quartz$\rightarrow$high-crystobalite transition). They belong among the order I transformations in the Ehrenfest thermodynamic classification.

Diffusionless mechanism is typical for many rapidly progressing polymorphic transformations. This is the mechanism of the martensitic transformations of metals and alloys [17]. They may occur also in oxide systems. Displacive or distortional polymorphic transitions according to the Buerger classification [18] also belong among them. The transformation tetragonal – monoclinic ZrO_2, and low – high cristobalite transitions are examples. They are order II or λ or higher-order transitions in the Ehrenfest classification [19].

This mechanism can not occur in its pure form. In oxide systems, the sublattice formed by the less-mobile oxygen anions undergoes little, correlated redistribution, whereas the mobile cations become displaced at greater distances. This mechanism may be called a diffusionless - diffusional one.

For many substances, the changes in several extensive properties as a function of the intensive thermodynamic parameters of state (pressure and temperature) accompanying phase transitions are as for order I processes, but others are as for order II or higher-order processes ('mixed-order processes' [20]). The substitutional disorder-order transformations of plagioclase, K-feldspars, pyroxenes and amphiboles are examples. They can be transitions with a mixed diffusionless – diffusional mechanism, and the shape of the characteristic functions is dependent on the contributions of diffusional and diffusionless displacements.

The above transformation mechanisms have been established for polymorphic transformations, but there is no reason why their operation during heterogeneous phase transformations in multicomponent crystalline and amorphous substances should be excluded. The diffusionless mechanism with a coherent interface allows obviation of the thermodynamic barrier to the formation of new phase nuclei. It can readily explain fast recrystallization processes such as spinel phase formation in metakaolinite, enstatite in sepiolite or serpentine crystallization, dehydrated colemanite recrystallization, etc.

Our recent studies have revealed the existence of complex reaction series in the Ca, Mg and alkali metal borates [21]. During heating, their structure undergoes rearrangement, which results first in the formation of the borates of Ca or Mg in an amorphous matrix formed by the borates of the alkali metals. At higher temperatures, the components take part in exchange reactions between the matrix and the crystalline borates formed earlier. Complex borates containing Ca or Mg and alkali metals according to the chemical composition of the parent substance are formed then.

The crystallization of many glasses takes a multistage course. In silicate glasses from the Li_2O–Al_2O_3–SiO_2 and MgO–Al_2O_3–SiO_2 systems, the first crystalline phase is often a quartz-like solid solution of a chemical composition close to the parent glass. At higher temperatures, its structure is rebuilt, with the formation of crystalline phases whose chemical compositions are increasingly closer to those of the stable thermodynamic phases (cordierite, spodumene, mullite, etc.). Several processes of multistage crystallization have been described in earlier studies [22, 23].

The phenomena of the formation of metastable phases and multistage crystallization are consequences of the specific structural features of a solid body as the medium of chemical processes. They result from the limited mobility of the component reagents, which changes with temperature. Only these chemical components which at the given temperature have the possibility to undergo rearrangement or displacement, determined for example by their diffusion coefficients may participate in the formation of new phases. The diffusion coefficients, of the components of the solid structure increase with increasing temperature, but the increases are different for the different chemical components. It may happen that at various temperatures different chemical components become capable of forming new compounds. Then, during the heating of a mineral, substances differing in chemical composition are successively formed.

The increase in the ability of the structural elements to undergo rearrangement with temperature can readily be observed in glasses. Up to the temperature of transformation of the glassy state (T_g), which corresponds to the viscosity 10^{13} dPas, glass behaves as a rigid and brittle body. A little above this temperature, it exhibits viscoelastic properties with rearrangement of large fragments of the network or/and structural units. When the temperature increase causes a reduction in the viscosity to 10^6–10^3 dPas, the glass displays the ability of viscous deformation, which accompanies the orientability of the structural units with the geometry of chains, spheroids and disc-like particles. With a further increase of temperature, the dimensions of these units diminish and accordingly the viscosity of the glass decreases.

At low temperatures, when the possibility of the rearrangement of the structural elements is limited, only those phases are formed whose chemical compositions and structures are the closest to the structure of the primary phase. Quartz-like solid solutions are formed in several silicate glasses, and calcium or magnesium borates in borates. These compounds do not appear in the diagrams of the phase equilibrium, or the chemical composition of the parent substance is found beyond the areas of their existence.

The crystallization of glasses in the Na_2O (10 mol%) – MgO (20 mol%) – $AlPO_4$ –SiO_2 system starts near the glass transition temperature (T_g), and aggregates of small, rounded grains of $AlPO_4$ are formed. At higher temperature, needles of $Mg_3(PO_4)_2$ besides $AlPO_4$ crystallize. Near the liquid temperature, only well-shaped dendrites of $AlPO_4$ appear. The change in the $AlPO_4$ morphology suggests a change in the crystallization micromechanism due to the increasing mobility of the components as the temperature is raised. Free diffusion favours well-shaped crystals; small, rounded grains are a result of short-distance rearrangements. The limited mobility in the low and middle-temperature range favours crystallization phases of complex composition and structure. The crystallization of fluorophlogopite from glass is an example. In the high-temperature stage of crystallization, simple compounds prevail.

The formation of structures similar to the parent structure is possible through small rearrangements in the anion network, similar to those which occur in the displacement or distorsional polymorphic transitions according to Buerger's classification or martensitic transitions in metals.

The formation of other intermediate phases requires more complex mechanisms, when a change in the anion network, usually less mobile, also has a diffusionless character, and the mobile cations become displaced at considerable distances in a diffusional mode. This represents an analogy to the disorder-order transformations in pyroxenes and feldspars.

With increasing mobility of the primary structure components, the proportion of diffusive displacements may increase, which will cause a corresponding change in the transformation mechanism.

In the diffusional stage of the process, due to the sufficient mobility of all chemical components, the formation of new compounds is determined by their chemical affinities. According to Prigogine and Defay [24], the free energy of the reaction is a measure of the affinity of the reactants. Accordingly, the compounds corresponding to the thermodynamic equilibrium state of the system are formed in this stage of the phase transitions.

In the low-temperature stage of the phase transformation, due to the selectively limited mobility of the components, the rate of reactant transportation becomes a governing factor. Compounds consisting of the most mobile components are then formed or diffusionless transformation takes place.

The action of chemical affinity as a factor determining the course of the reaction is strongly modified here by the mobility of the components. Thus, the micromechanism of the intrastructural phase tansformations is dictated to a considerable degree by the freedom of the components to undergo rearrangement.

Chemical bond strengths and thermal stabilities of solids

The strengths of the chemical bonds, together with the freedom of the reagents which to a considerable extent depends on them, determine the courses of thermal processes and the thermal stabilities of solids.

The theory of chemical bonds and determination of their strengths are the subject of quantum mechanics. However, the problem is complicated that up to now it has been solved satisfactorily only for the H_2 molecule.

A knowledge of the actual values of the strengths of the bonds in the complex structures of solid bodies is still lacking. Their magnitude is estimated approximately by using as a measure of atomic interaction simple values such as the ion electric charges (Z) and the ion radii (r), Cartledge's cation field strengths (Z^2/r) [25], Dietzel's ion potentials (Z/r) [26] or Pauling's electronegativity values.

Attempts have been made to correlate the thermochemical properties of a substance with the radii and the charges of ions or the strengths of ionic fields expressed by means of ionic potentials. Several interesting functional relationships have been obtained for simple substances. They are based on the assumption that the interaction at higher temperatures between two ionic compounds with a common anion, e.g. two oxides or halides, depends on the difference in the geometric (radius) and energetic (field strength) features of the cations [26–28].

Dietzel made use of such a relation with reference to silicate melting and the crystallization of glasses. Interesting advances in this field are due to the studies of Świętosławski, Penkala and Görlich on the interdependence of the crystallochemical properties of ions and solid solutions or eutectic formation in binary systems with a common anion [29–31].

It has been shown by Cartledge that the ionic potential function can serve to correlate numerous properties of compounds, such as the acid-base character of hydroxides and the physical properties of chlorides. He demonstrated that functional dependences exist between the enthalpies of formation for simple oxides, halides, carbonates, nitrides and some other salts and the values of the ionic potentials of the cations forming these compounds [27].

As observed by Stoch [32] for binary and ternary oxide systems, the lowering of the melting temperature of an oxide due to the presence of a second oxide (ΔT), as indicated by the appropriate liquidus curve, is a function of the ionic potential of the cation of the second oxide:

$$\frac{\Delta T}{n_2} = a\frac{1}{\varphi_2} + b$$

where $b \doteq 1/\varphi_1$, φ_1 is the ionic potential of the cation of the dissolving oxide, and φ_2 is the ionic potential of the cation of the second component, while n_2 is its molar fraction.
Coefficient a is positive for cations having $1/\varphi$ larger than that of the cation of the dissolving oxide, and negative for those having $1/\varphi$ smaller.

This means that the solubility of an oxide in a binary melt is approximately proportional to the difference of the reciprocals of the ionic potentials of the cations of the two oxides. When several substances may crystallize from a given melt, the first to crystallize should be that for which the mean reciprocal of the ionic potentials of its cations is nearest to that of the melt [32].

The relations described above [32] and also those derived by Cartledge [27] have the shape of two straight lines intersecting in one point (V-shaped diagrams). This can be explained as follows: One of the lines is produced by weak field strength cations; in a two-component system, they influence the properties of the system by breaking the anion sublattice in the structure of the solid. The other line is determined by high field strength cations. These weaken the chemical bonds inside the ligands or in the coordination polyhedra formed by the coexisting cation, depolarizing these bonds. This changes the properties of the given compound or system. The decrease in the decomposition temperatures of carbonates as the cation field strength increases is an example.

In inorganic and physical chemistry, electronegativity is universally accepted as a standard characteristic of elements and cations. Electronegativity values were calculated by Pauling, but the low precision of these values limits their practical application.

A new factor characterizing the crystallochemical properties of cations and atoms has been introduced by Görlich. This is the effective nuclear change of the atomic core, defined as $Z_{eff}=\sqrt{I_v'}$, where I_v' is the ionization energy in Rydberg units needed to remove the last valency electron from an atom. It is closely related to Pauling's electronegativity, but is much more precise both in its physical meaning and in its particular values [33, 34].

The effective nuclear charges of atomic cores order chemical elements according to the specific character of their homeopolar bonds [34]. The relative difference in the nuclear charges of two bonding atoms constitutes the factor deciding the ionicity of a heteropolar bond. Ionicity is a nonlinear function of the mean covalency of the bonds [35].

The Z_{eff} and i values constitute a direct measure of the Lewis acidity of atoms and cations [36]. They show a good correlation with the thermal stability of inorganic compounds and with many other properties of the compounds [33].

The present-day spectroscopy of solid bodies, which allows determination of the strength constants of chemical bonds (IR spectroscopy), permits the hope that accurate quantitative experimental data on bonds can be obtained.

In the oxides, the interaction between the oxygen and the surrounding cations is characterized by its alkalinity. The alkalinity, the capacity of the oxygen atom to transmit negative charge to the cations surrounding it, is a measure of the covalence of the oxygen – metal bonds. The acid-base relationship has also been applied in the theories of the glassy state and of the phenomena occurring in oxide glasses and in melts. Their alkalinity is determined from spectroscopic bond shifts (optical alkalinity [37, 38]).

X-ray photoelectron spectroscopy appears to be very well suited for characterization of the electron densities of the structural elements of solids. It is able to provide specific information concerning the charge variations resulting in the particular atoms from changes in the valency or local structure, and atom core binding energies for metals and oxygen can be measured.

The amount and the reliability of data obtained by means of these new, modern methods will continue to increase, which will impart an increasingly quantitative character to the structural and crystal-chemical analysis of the processes.

The decomposition temperatures of many inorganic compounds change appropriately in conformity with the crystal-chemical parameters of the elements which make up these compounds. This is especially clear for complex compounds, as demonstrated by Cyganski *et al.* [39–40].

For example, the temperature of the endothermic DTA peak onset for the decomposition of the nitritolanthanates of silver, $M_2Ag[Ln(NO_2)_6]$ (where M=Cs, Rb and Ln=lanthanides), decreases with decrease of the lanthanide cation radius [39]. The same trend is demonstrated by the lattice constants of these compounds. Among the compounds containing the same central ion and different outer sphere cations, a decrease in the cation radius of the potassium group elements results in a decrease in thermal stability [40].

The temperature of the beginning of the decomposition of alkali metal nitrocuprates(II) increases with increasing ion radius of the outer sphere cation. The strength of the bonds of the appropriate cation with the complex anion increases in the same direction, which is demonstrated by the appropriately diminishing distance between this cation and the copper in the anion [41].

Similar regularities can be observed in the activation energy values for the decomposition of complex nitrobismuthates [42].

Interesting dependences of the temperature and the activation energy of decomposition can be found in thiocyanatobismuthates(III). The most stable mononuclear complexes are those containing chloride ligands. Complexes with bromide ligands exhibit lower stability, and those with iodide ligands are the least stable. With increasing radius of the halide ligands, the stability of mononuclear complexes decreases, while that of binuclear complexes increases [43, 44].

Relations between the structure of the anion and the thermal decomposition of complex Bi, Pb and Sb halogenide salts were described by Ptaszynski [45–47].

The interdependences presented here allow prediction of the thermal stabilities of new complex compounds.

The multi-stage decomposition of salts and the succession of the formation of the transition compounds can be predicted on the basis of acid-base interactions. For purposes of quantitative determination of the acidic properties of cations, Gontarz and Górski [48] introduced the electronegativity force (E_f). This is expressed by the function

$$E_f = \frac{-E_j}{r}$$

where r is the cation radius for the coordination number 6, and E_j is the energy of the last degree of atom ionization leading to the formation of the cation under consideration.

This quantity, however neglects the polarizability of the ions and the varying coordination numbers of the cations.

The electronegativity force expresses the energy of binding of the first electron by the cation. Through the use of this concept, it was possible, among other things, to determine precisely the decomposition stages of sodium hyposulfite $Na_2S_2O_5$ and other oxo salts, by separating the stages into elementary acts, which would be difficult by means of experiment [49–51].

It should be remembered that in the case of cations of the same group of the periodic table, whose ionization energies differ little from each other, the multiplicity of the electronegative force, i.e. the acidic properties of the cations, depends mainly on the ionic radii. This accounts for the dependence observed between the thermal properties of the compounds and the ion radii.

Final remarks

Many thermal reactions of minerals and inorganic materials are processes involving rearrangement of the internal structure elements. Their micromechanisms are dictated by the strenghts of the chemical bonds of the components and the freedom of their displacement.

A knowledge of the crystal-chemical properties of the cations or atoms constituting this structure and the freedom of their displacement is indispensable for a recognition of the actual thermal process mechanism and the direction of its progress, which is presented in the paper.

The crystal-chemical approach used here is complementary to the conventional thermodynamic and kinetic studies of phase transformations. It takes into account the real nature of thermal processes of minerals, facilitating an understanding of the role of particular components of the mineral structure in the thermal process and prediction of the course of thermal transformations of minerals.

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