

INTERDEPENDENCE BETWEEN THE DISPERSION OF A SOLID DECOMPOSITION PRODUCT AND ITS FORMATION RATE

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In an analysis of the possible mechanism and kinetics of a thermal decomposition reaction with the formation of a solid product, the following features were considered: the collective rearrangement character of the transformation; the formation of a product with a different non-equilibrium defectiveness and free energy; the free energy relationship in the series of processes leading to products with different dispersions; the formation of intermediate structures; and the spinodal character of their decomposition. Relationships are presented between the rate of solid product formation, the process temperature, and the surface area and size of the particles.

The degree of dispersion is one of the main distinctions between an inorganic material and a compound. From this point of view the possibility of dispersion control in the course of a chemical reaction is of great importance for material science.

The aim of this work is to determine the interdependence relations between some kinetic parameters and conditions of a solid decomposition reaction and the dispersion of the product formed.

It is assumed that the theory of topochemistry is able to describe the dispersion of reaction products. Having determined the laws of formation, development and overlapping of the nuclei of a new phase, one can evaluate their size distribution at any time and under any conditions of the process investigated. However, this is valid only in the event of the monocrystallinity of the nuclei. As a rule this is not the case in topochemical reactions of practically importance.

One of the possible mechanisms of topochemical reactions

It is assumed, and in some cases it is demonstrated, that in the process of thermal decomposition of solids intermediate pseudostructures are formed. Examples are a decomposition product with the unstable structure of the initial compound, or a solid solution of the product in the initial compound. The product particles are formed in the process of destruction of this unstable intermediate structure. X-ray phase investigations have provided evidence that the pseudostructure decomposition associated

with the crystallization of a new phase gives rise to a sharp increase in the surface area of the product [1].

The destruction of the intermediates mentioned is presumed to proceed by collective rearrangement of the lattice atoms [2]. Use of the methods of non-equilibrium thermodynamics for examination of the process of destruction of these intermediates was proposed in [3]. Barret [4] first discussed the formation of the final product from the intermediate as the spinodal decomposition of a solid solution. It is assumed that the fluctuations in the thermodynamically unstable system can appear in the form of waves of density of the components, covering regions much larger than the wave period. Under certain thermodynamic conditions the diffusion processes are directed along the concentration gradients and result in the space ordering and the separation of the system components [5].

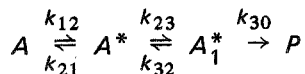
We use the free energy relationship to connect the thermodynamic characteristics of the product and the kinetic parameters of its formation. It is known that in a series of similar processes there is a relationship between the free energies of activation and the free energies of the final state [6, 7]. The linear-type relationships

$$\Delta G^* = \alpha \cdot \Delta G + \beta$$

where ΔG^* is the free energy of activation of the reaction, ΔG is the free energy of the final state, and α and β are constants, are known as Polanyi relationships.

Kinetic scheme of the process and its analysis

We describe the thermal decomposition $A \rightarrow P$ as the sequence of stages in the reaction zone:



where stage 1 is the chemical stage of formation of the intermediate pseudostructure in place of part of the initial crystal; stage 2 involves the space ordering of the components, leading to the periodic structure of the concentrations and the corresponding of the strains; and stage 3 entails the irreversible destruction to particles of product, the morphology of which is related to the ordered structure. A , A^* , A_1^* and P are parts of the crystal with the size of the final product particles.

Formally analogous kinetic schemes have been investigated in other physico-chemical processes [8]. Using the usual approximation of the stationarity of the concentrations of A^* and A_1^* , one can describe the experimentally determinable rate constant of the product formation as

$$k_p = k_{12} / (1 + k_{21}/k_{23} + k_{32}k_{21}/k_{23}k_{30})$$

Since

$$k_{23} = k_{23}^0 \exp(-\Delta G_{23}^*/RT)$$

$$k_{32}/k_{23} = \exp(\Delta G_{23}/RT)$$

we obtain

$$k_p = k_{12} / [1 + (k_{12}/k_{23}^0) \exp(\Delta G^*/RT) + (k_{21}/k_{30}) \exp(\Delta G/RT)]$$

Taking into account the constancy of k_{12} , k_{21} , k_{23}^0 and k_{30} during the variation of the product dispersion, we obtain that k_p is dependent only upon ΔG_{23} and ΔG_{23}^* .

Further, we analyse the real values of the terms on the right side of the equation obtained. We assume that the main contribution to the increase in the product free energy is one connected with the surface formation. The real value of ΔG_{23} is less than 10 kcal/mol. The value of ΔG_{23}^* can be some tens of kcal/mol. The equation is then transformed into

$$\log k_p = \log(k_{21}k_{23}^0/k_{12}) - \Delta G_{23}^*/2.3 RT$$

From the Polanyi expression we obtain the main relationship between the rate constant of solid product formation and the product free energy:

$$\log k_p = -\alpha' \cdot \Delta G_{23} + \beta'$$

If ΔG_{23} is directly proportional to the product surface area S , then

$$\log k_p = AS + B$$

where A and B are constants. For cubic particles with edge d :

$$\log k_p = A'/d + B$$

The ordering process has a diffusion character and is thermally activated. If the thermal dependence of k_p is of Arrhenius form, we obtain for the temperature T_0 and T :

$$(1/T_0 - 1/T) = \text{const} (S_0/T_0 - S/T)$$

For small ΔT :

$$(1/T_0 - 1/T) = \text{const} (S - S_0)$$

or

$$(1/T_0 - 1/T) = \text{const} (1/d - 1/d_0)$$

Discussion

For a topochemical reaction of thermal decomposition with the formation of an unstable intermediate structure, therefore, one can define the relationships between the effective rate constant of product formation and the temperature of the process, and the free energy or the size of the particles formed.

Analysis of the presented mechanism and of the relationships obtained permits prognostications for this type of reactions as concerns effects which are of importance for the experimenter:

a) In topochemical reactions the process of space ordering of the intermediate structure can be observed, e.g. through the appearance of superstructural reflexions in the X-ray pictures and electronograms.

b) The experimentally determined effective rate of solid product formation, e.g. the optically observed rate of movement of the reagent-product interface, is related to the size of the forming particles; an increase in the rate of product formation (before the temperature of sintering) leads to a decrease in particle size.

c) There is a relationship between these parameters, e.g. between the temperature of the process and the particle size. Thus, the experimental definition of such relationships receives a semiquantitative basis.

References

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Zusammenfassung — In einer Analyse des möglichen Mechanismus und der Kinetik einer unter Bildung eines festen Produktes verlaufenden thermischen Zersetzungsreaktion werden folgende Besonderheiten erörtert: der kollektive Umordnungscharakter der Umwandlung, die Bildung eines Produktes mit unterschiedlicher Nichtgleichgewichts-Gitterstörung und unterschiedlicher freier Energie, die Beziehung der freien Energie in zu Produkten unterschiedlicher Dispersität führenden Prozessen, die Bildung intermediärer Strukturen und der spinodalen Charakter ihrer Zersetzung. Beziehungen zwischen der Bildungsgeschwindigkeit des festen Produktes, der Temperatur des Prozesses und der Oberflächengröße und Größe der Partikel werden angegeben.

Резюме — В анализе механизма и кинетики реакции термического разложения с образованием твердого продукта рассмотрены следующие положения: коллективный характер превращения; образование продукта с различной неравновесной дефектностью и свободной энергией; корреляционное соотношение свободных энергий активации в рядах процессов, приводящих к продуктам с различной дисперсностью; образование промежуточных структур и спиnodальный характер их распада. Предложены корреляционные соотношения между скоростью образования твердого продукта реакции, температурной превращения и площадью поверхности, размерами частиц твердого продукта.