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INFLUENCE OF SOME FACTORS ON THERMAL DISSOCIATION OF SOLIDS

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ABSTRACT

The influence is shown of the size of solid grains of a reaction substrate; their size reduction; distribution of solid grains; the range of their transformation and the porosity of a solid layer formed on substrate grains during reaction, on the course of reaction. The method of interpreting research data, possibility of their mathematical description and evaluation of kinetic parameters of endothermic dissociation reactions are also discussed.

INTRODUCTION

In processes with solids, reactions of thermal dissociation are a separate group. In such reactions solids are transformed and gaseous and solid substances result from them.

By testing kinetics of these processes we mean the identification of intermediate and final products of dissociation, determining the process rate and its kinetic parameters, and establishing the influence of solid state parameters on the course of a process.

Thermal dissociation depends on many internal and external factors [1] . The internal factors regarded as the most important ones are: the scope of energy of substrates and reaction products; mobility of crystal lattice elements; amount of energy affecting the graining process of reaction substrates which can also be an external factor ; lattice defects; Hedvall effect; similarity of substrate structures and reaction products, and others.

The external factors regarded as the most important ones are: temperature; reaction time; pressure and composition of a gaseous phase; presence of additives and catalysts, and others.

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Some of these factors can be controlled [e.g. graining of substrates, distribution of grains according to their size, temperature, reacting time, pressure and composition of a gaseous phase] . It is also very important to find a way of interpreting research data such that the used mathematical method could represent the physical state of an analyzed process.

In this paper a synthetic assessment of some of the above-mentioned factors and a possibility of interpreting research data are shown.

RESULTS AND DISCUSSION

Kinetic equation: refers as usual to the defined model of a reacting composition. Such an equation should meet at least two basic conditions:

(1) - describe an elementary process limiting observed reaction rate, and

(2) - describe the whole scope of a change with points of interval [$\alpha = 0$ and $\alpha = 1$] as well. Examples of such equations are:

$$1 - \left[1 - \alpha\right]^{1/3} = k'.\ t \qquad [I]$$

$$\left\{1 - \left[1 - \alpha\right]^{1/3}\right\}^2 = k''.\ t \qquad [II]$$

[where: α = scope of a change; t - time; k', k'' - constants proportional to the permanent reaction time] .

These equations describe the shifting rate of a limit of solid phases between the product and the substrate in the kinetic [I], and the diffusion [II] process range. The advantage of these equations is that there is only one constant value in them. Kinetic equations with more constants can describe research data very well but it is usually difficult to find a physical interpretation for these constants.

Other factors: if, in the kinetic equation one cannot avoid introducing other factors then one should define them thoroughly giving them a definite physical sense [the mixed one is the best] , appropriate for the process being described. You cannot introduce, for instance, the idea of a reaction order into equations describing topo-chemical processes because in these processes such a value has no physical sense.

Distribution of grain sizes has a definite influence on the description of research data. In polydispersed material after time "t" the scope of change is different for grains with different initial sizes.

The average value of the scope of change can be described by the relationship:

$$\overline{\alpha} = \int_{r_i=0}^{r_i = r_m} \left[1 - \alpha/r_i/\right] \varphi/r/ \, dr \qquad [III]$$

[where: r_i = initial radius of grain "i" of this fraction; r_m = initial radius of a grain of the largest fraction in the tested sample; $\alpha[r_i]$ = scope of change for the fraction with radius "r_i"; $\varphi[r]$ = frequency function of grain sizes].

Transforming equations [I] and [II] and introducing into them frequency functions of the most often met distributions: the regular one and the Rosin-Ramler one, one can obtain relationships describing the average scope of change:

[a] for regular distribution:

$$\overline{\alpha} = 1 - \left\{ \left(\frac{B}{\pi}\right)^{1/2} \int_{\theta_1}^{\theta_m} \left(1 - \frac{\theta_1}{\theta}\right)^3 \cdot \exp\left[-B\,(\theta - 1)^2\right] d\theta \right\} \qquad [IV]$$

[where: $B = \frac{r^2}{2\sigma^2}$; σ = variance, $\theta = f\left[r_z = \frac{r}{\bar{r}}\right]$; $\bar{r}$ = average radius of substrate grains];

[b] for Rosin-Ramler distribution:

$$\overline{\alpha} = 1 - \left[\int_{\theta_1}^{\theta_m} \left(1 - \frac{\theta_1}{\theta}\right)^3 \cdot \theta^{n-1} \cdot \exp\left(-\theta^n\right)\right] dO \qquad [V]$$

[where: n = parameter characteristic for sizes of distributed grains].

Analysis of kinetic curves obtained as a result of a numerical solution of the relationship [IV] and [V] by means of initial equations [I] and [II], shows that in the case of the regular distribution the process can be described only with the equation [I] and only for $B \geqslant 20$, e.g. for $\sigma \leqslant 0.158$, but in the case of Rosin-Ramler distribution only with the equation [II] and only for "n" close to one, e.g. when distribution approaches the exponential distribution. Thus the type and character of distribution of sizes of grains should be taken into account when analyzing kinetic data.

Omitting [r] in the kinetic equation can lead to a trivial description of research data by means of the diffusion equation with high value for activation energy so characteristic for a kinetic region of reaction.

Influence of self-reduction of grain sizes: such a process can be observed, for instance, during dissociation of various grain fractions of natural calcite. The linear relationship between "k" and "$1/r_i$" [3], results from the equation [I]. In Fig. 1 it was shown that such a relationship is not observed probably because of the initial range of dispersion caused by self-reduction of grain sizes of the substrate during reaction; this process does not lead to the increase of the number of grains but depends on deep cracking of grains in which quite wide gaps occur. As a result of this [4], instead of the relationship $k = f\left(r_i^{-1}\right)$ one can observe the relationship $k = f\left(r_i^{-\frac{1}{2}}\right)$ [Fig. 2].

Influence of a small layer of a solid reaction product which appears on the substrate grain is often observed and can influence the evaluation of kinetic parameters.

During dissociation of thick-crystal fraction of a natural calcite $d_{25} = 1.73$ and 3.46 mm at temperatures above 900°C there can be observed the increase in rate [Fig. 3] caused by resistance of CO_2 diffusion in the CaO layer forming on the $CaCO_3$ grain when the CaO layer achieves a proper thickness, e.g. for $\alpha > 0.8$.

The parameter of CaO regular lattice [2.4 Å] is almost 1.5 times smaller than the lattice constant [4.0 Å] of a trigonal calcite; so that the considerable relative porosity of CaO equalling 54% [6] does not create any serious resistance; increase in CO_2 pressure in the reaction zone is small and, as a result of this, Arrhenius energy of process activation decreases.

Another influence of a small layer of a solid reaction product can be observed during dehydration of crystalline hydrates of tripolyphosphates [7] .

In the early stage [$\alpha < 0.5$] there is a quick loss of water and value "E" is constant. The further course of the process is clearly delayed and for $\alpha \cong 0.5$ the layer thickness of a product increases to such a degree that disposing of a gas

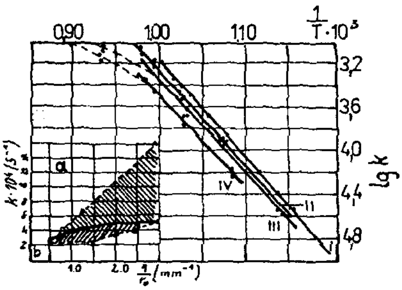

Fig.1. Relationship between lg k and 1/T and between k and $1/r_o$ [a] for four fractions of natural calcite.

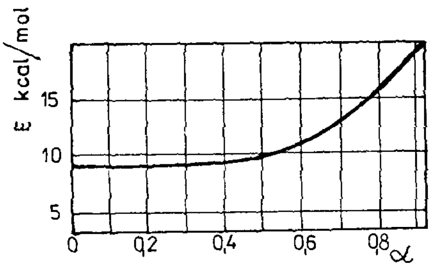

Fig.2. Relationship of Arrhenius activation energy and the scope of change for dehydration of $Na_3NiP_3O_{10}\cdot 12H_2O$.

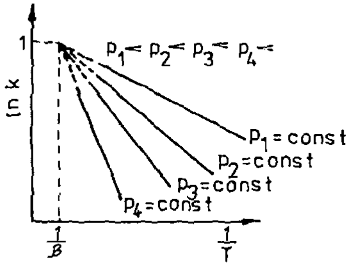

Fig. 3. Zawadzki – Bretsznajder's relationship and isokinetic temperature [β]

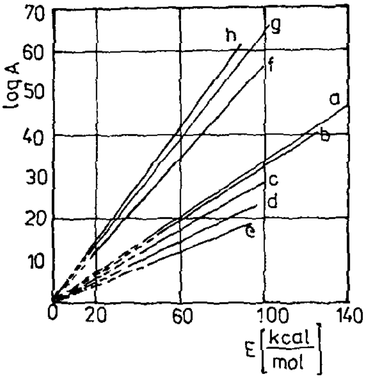

Fig.4. Compensation effect for some carbonates [a – e] and tripolyphosphates [f – h]

product is difficult; the pressure of water vapour in the reaction zone increases greatly and reaction reaches the diffusion phase in which Arrhenius energy of process activation increases gradually [Fig. 4].

Compensation effect and isokinetic temperature represent the so called correction due to thermal dissociation of solids. Another correction of thermal dissociation is Zawadzki-Bretsznajder relationship [8].

$$E = f\,[p_i] \qquad [VI]$$

[where: p_i = pressure of gaseous reaction product].

The existence of the so called isokinetic temperature results from the relationship [VI].
The relationship called the compensation equation:

$$\ln A = a + b \cdot E \qquad [VII]$$

[where: "a" and "b" = constants] describes the increase of Arrhenius activation energy [E] which cannot be compensated for by a temperature increase; this leads to increase in the value of a non-compensation factor [A] in the Arrhenius equation.

In this paper there is presented a view in which only the pencil correlation of the type of Zawadzki-Bretsznajder relationship can have a physical sense. The deviation factor of this correlation is the value of the gaseous pressure of the reaction product [p_i], and the consequence of the relationship [VI], is the so-called isokinetic temperature which is a hypothetical value that has never been obtained during testing of thermal dissociation of solids.

The compensation effect expressed by the equation [VII], represents another way of presenting the relationship [VI], which is connected with mathematical duality of correlative relationships resulting from the Arrhenius equation treated as a special case of a projection line.

CONCLUSIONS

The review of a few very important factors influencing the thermal dissociation of solids leads to the conclusion that the shape of a process model depends on the researcher's intentions who while creating the model takes into consideration many different factors for various reasons. These factors should be always given a suitable physical sense. In creating the mathematical process model one should carefully analyze the physical and mathematical properties of a selected model.

Many problems can be avoided in interpretation by generalization of kinetic data with the criterion relationship [11], which enables elimination of kinetic parameters difficult to determine and describe. The criterion relationships are also known and used in processes here discussed [12].

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