A STUDY ON THE PROPERTIES OF REACTIONS WITH SOLID PHASE PARTICIPATIONS

Cristina Damian

„Ştefan cel Mare" University of Suceava, Faculty of Food Engineering, Universităţii 13, 720225, Suceava, ROMÂNIA

Abstract: *The main aim of this paper is a general presentation of the properties of reactions with solid phase participation.*

There have been presented some a general classifications of these reactions and the methods for their analysis used in some investigations (thermogravimetry, derivative thermogravimetry and differential thermal analysis).

Keywords: *thermal methods, nucleation, thermogravimetry, differential thermal analysis.*

Introduction

Recently, kinetic studies of reactions with solid phase participations have developed enormously, regarding the contributions to the settlement of some important issues in contemporary chemistry.

These reactions are characterized by total destruction, during the process, of the characteristic phase of the reacting substance, and the beginning of a new phase, specific to the reaction product. The reactions propagates from the nuclei that appear on the solid surface, followed by a growth, the reaction rate being influenced by the number, shape and size of the germs. In the case of these reactions there is a competition between two processes: a chemical one, and a physics process: diffusion. The rate of the whole process will be determined by the slowest process, taking into account, in this case, the importance of the transportation issue (Isac, 1994). When the diffusion rate is low, the overall rate will be controlled by the diffusion field, and vice versa. Because of this, kinetic parameters have no longer a precise meaning, ad in the case of homogeneous reactions, the reaction order and activation energy being characteristic to an overall process at a given moment of the reaction and transformation order, respectively.

Classification of reactions with solid phase participation

Reactions with solid phase participations are quite varied, which creates difficulties when classifying them.

One of the classifications which is worth mentioning refers to phases which react or result from reactions (Šestak, 1973). Taking into account this criterion, we can distinguish the following types of reactions:

- Reactions in solid-gas system (decomposition of some solid bodies or mixtures of solid bodies with volatile compound escape);
- Reactions in solid-liquid system;
- Reactions in solid-solid system.

Another classification of reactions with solid phase participations, which is very useful for the kinetic description and suggests some elements regarding the mechanism evolution, is presented in figure 1 (Murgulescu, 1960).

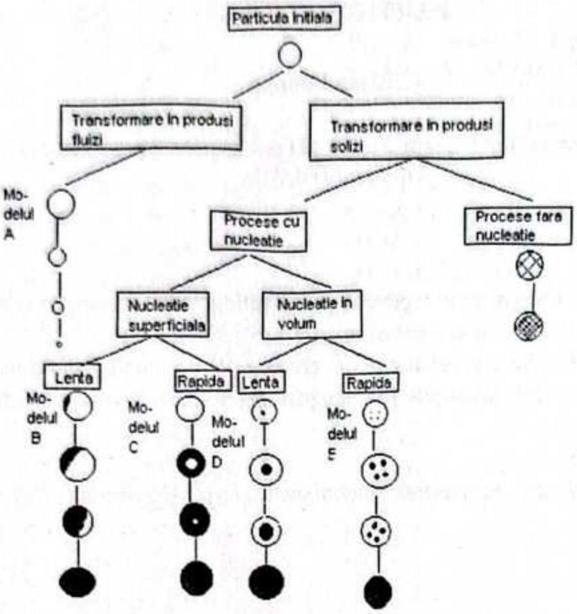

Figure 1 Classification of reactions with solid phase participation.

An important number of reactions of solid bodies take place in the certain regions of the network creating areas consisting of a small number of molecules of the reaction product, called germs or nuclei. Their formation process is called nucleation. Nucleation can take place at the surface or in volume, slowly or fast. The classification of solid bodies reactions presented in figure 1 contains a sub-classification of nucleation processes which appear in their evolution. The models for the solid reaction presented describe both the reactions of a single solid phase (such as the decomposition reactions with a volatile compound escape), and the reactions in which solid reacting substances are associated with other reacting substances in any aggregation state. In the latter case, it is assumed that one of the reacting substances consists of corpuscules with such a small size that it becomes a dispersion medium for the latter.

For example, general reactions

$$A(s) + B(fluid) \rightarrow AB(fluid) \quad (1)$$

fit into model A, while reactions with general forms

$$A(s) + B(fluid) \rightarrow AB(s) \quad (2)$$

$$A(s) + B(s) \rightarrow AB(s) \quad (3)$$

correspond to model C.

For the description of the evolution of the last two categories, the image of a continuous process seems to be quite useful, a process in which the reacting substance B is adsorbed on the grains of the reacting substance A, whose volume change continuously to the volume of the reaction product.

Finally, the branch on the right extremity of figure 1 refers to processes with solid phase participation which take place without nucleation (such as the ordering ones).

A final model of solid body reactions (model F) which is not presented in figure 1, refers to reactions between solids having grains of comparable size. According to this model worked out by Komatsu, reactions only take place in contact points of the crystalline grains supposedly spherical (Damian, 2006).

An important group of reactions with solid phase participation is the decomposition of solids. This type of reactions can be represented by the general chemical equation:

$$\nu_A A(s) \rightarrow \nu_B B(s) + \nu_C C(g) \qquad (4)$$

reaction type in which thermal decomposition of carbonates, oxides, complex combinations, abstraction of water, etc., are also part of, and whose study is important both for practical and theoretical reasons.

In order to emphasize the character of location of the reactions area in certain regions of the crystals, the reactions with solid phase participation in general, and the reactions of decomposition of solid bodies in particular have been named topochemical reactions.

The kinetic equations does not include the influence of different parameters, that is why there are disparities among the kinetic parameters obtained through different methods and a strong variation of these values with experimental conditions and characteristics of the sample, which explains the number of evaluation methods for kinetic parameters that we come across in the literature, out of a desire to evaluate using high precision methods.

Thermal analysis methods are preferred for the investigation of these systems; they are based on the study of a physical property of the system analised according to time or temperature.

We mention the fact that, at the same time with isothermal methods for determination of kinetic parameters, anisothermal methods have been developed, the latter are faster and their thermal behaviour can be pursued at a temperature range of 25^0C – 1500^0C.

Thermal methods for analysis

The thermal methods of analysis include a group of techniques related which measure the temperature dependency of some parameters or properties specific to the sample.

The assimilation of a large number of experimental data and the appearance of more variants of one and the same working technique imposed the necessity to standardize working conditions and homogenize terminology.

The most used thermal methods for the investigation of reactions with solid phase participation are: thermogravimetry TG, derivative thermogravimetry DTG and differential thermal analysis.

The principle of the thermogravimetric method and the characteristics of TG and DTG curves.

Thermogravimetry TG is a dynamic technique which allows the measuring in time or according to the temperature, of a sample weight, heated or cooled according to a schedule (USER-COM, 1998).

$$w=f^*(T \text{ or } t) \qquad (5)$$

The experimental graph or mass loss depending on temperature is called thermogram and has the following characteristics:

- The segment AB is the part of the TG curve in which the sample weight remains almost constant;
- The initial temperature T_i, at which degradation begins;
- The final temperature T_f, which is the point in which the mass variation is at maximum;

The reactions interval is: T_i-T_f

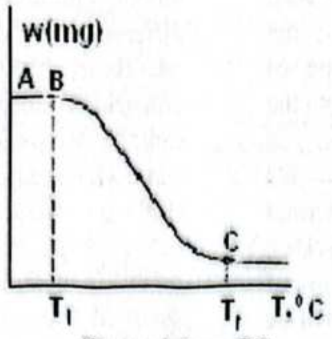

Figure 1 Curve TG.

In figure 2 there is a thermogram which presents three degradation stages:

a) a first stage which represents an initial low mass loss (w_0 – w_1), and which results from the solvent desorbtion – if it takes places at about 100^{0}C this can be explained by water loss;

b) a second stage (w_1 – w_2) – and sometimes a third stage (w_2 – w_3) – which are results of the thermal decomposition of the sample.

The DTG curve, be it mathematically derivated or directly recorded, does not contain more information than an integral TG curve obtained in the same experimental conditions. Auxiliary devices are valid for most thermal balances, i. e. DTG curves can be easily recorded with TG curves. They can also establish the corresponding temperature of the maximum degradation speed.

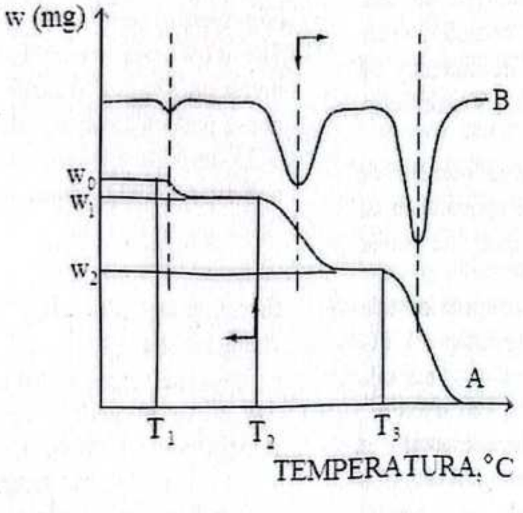

Figure 2 Thermograms: A – thermogravimetric curve TG;
B – derivative thermogravimetric curve DTG (w – weight loss of the sample)

The most important problems in thermal analysis are the constant speed of temperature change and the temperature measurement. The temperature sensor should be in contact with the sample, even if this creates inconveniencies. Commercial thermobalances have a timed heating temperature and gas atmosphere. Most systems display derivative TG curves, and part of them have a computer for temperature programming and extraction and analysis of data (THERMAL ANALYSIS, 2000).

The principle of the differential thermal method and the characteristics of the DTA curve

The differential thermal analysis (DTA) is a dynamic techniques which allows the recording of the temperature difference between the sample analized and a reference substance dependending on time / temperature. Both samples, the analized one and also the reference one are in the same enclosure and they are subject to heating according to a programme set by temperature. Data recording is based on the representation on the ordinate of the ΔT and of time or temperature on the abscissa.

The interpretation of curves is difficult and it often depends on extra information obtained from other analytical methods.The coupling of these methods led to multifunctional, which offer the possibility to characterize the sample analized in the same conditions using more thermal methods.

Recently, multifunctional devices include mass spectrometer, which offers informations referring to divided fragments during the analysis, depending on time/temperature. Modern devices also allow automated kinetic processing (Hurduc, 2002; Hurduc, 2004).

Conclusions

The study of reactions with solid phase participation brings contributions to the solving of some important issues of modern chemistry, offering information regarding the thermal stability of substances, the possibility to control synthesis processes in order to obtain some materials with desired properties and also helping clear up the degradation mechanism.

At the same time, the results allow the optimization of productions processes, in general, and of the polymeric materials, in particular.

The study of thermal degradation mechanism of macromolecular compounds contributes to the solving of important current problems regarding the polymeric waste recycling, with the reinstatement in the industrial circuit of some degradation products.

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