DETERMINATION OF THE KINETIC PARAMETERS
OF THE MULTI-STAGE THERMAL DECOMPOSITION OF SOLIDS
UNDER NON-ISOTHERMAL CONDITIONS BY THE NON-LINEAR
ESTIMATION APPROACH

A MODEL OF ALUMINIUM HYDROXIDE DECOMPOSITION

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(Received April 1, 1978 in revised form March 7, 1979)

The activation energy of decomposition of aluminium hydroxide vs. weight loss was
estimated from thermogravimetric data collected over a wide range of heating rates,
without resorting to the model of the reaction mechanism.

These activation energy values were subsequently used to distinguish individual
dehydration stages and to determine the best models of the reaction kinetics for these
stages.

Finally, the overall decomposition model was formulated, and its parameters were
determined by the non-linear estimation approach.

Owing to the development of numerical, computer-based identification method,
derivation of a model for the multi-stage thermal decomposition of a solid has
become a greatly simplified task [1]. However, a suitable procedure for processing
of experimental data to obtain the most information possible on the individual
decomposition stages remains of significance. Such a procedure should help to
establish a preliminary model structure and determine the activation energy values
for the individual stages.

Here, a method is advanced for determining the activation energy and the model
structure for the individual thermal decomposition stages, and for developing
a kinetic model of overall decomposition that would most accurately account
for the experimental data over a wide range of experimental conditions.

Theoretical

In the multi-stage thermal decomposition of a solid under increasing tempera-
ture it often happens that the successive stages of the process overlap rather than
proceed separately.

Depending on the decomposition mechanism involved, the chemical reactions
corresponding to the individual stages can occur either consecutively or simulta-
neously.
a) Consecutive pattern
\[ A_s \rightarrow B_s + C_g \]  
\[ B_s \rightarrow D_s + E_g \]  
stage I  
stage II  
\[ (1) \]

b) Parallel pattern
\[ A_s \rightarrow B_s + C_g \]  
\[ F_s \rightarrow G_s + H_g \]  
stage I  
stage II  
\[ (2) \]

The weight loss of the sample undergoing decomposition can be expressed in terms of the conversion degrees achieved in the individual reactions, according to the formulas

\[ a) \quad y = m_c + m_E = m_0(K_1\alpha_1 + K_2\alpha_2) = K_1\alpha_1 + K_2\alpha_1\alpha_2 \]  
\[ (3) \]

where \[ \alpha_1 = m_C/m_{C_{\infty}}; \quad \alpha_2 = m_E/m_{E_{\infty}} \]
\[ K_1' = M_C/M_A; \quad K_2' = M_E/M_A \]
\[ K_1 = m_0K_1'; \quad K_2 = m_0K_2' \]
\[ m_{C_{\infty}} = m_0M_C/M_A; \quad m_{E_{\infty}} = m_CM_E/M_C \]
\[ m_0 = m_{A_0} \]

\[ b) \quad y = m_c + m_H = m_{A_0}K_1'\alpha_1 + m_{F_0}K_2'\alpha_2 = K_1\alpha_1 + K_2\alpha_1\alpha_2 \]  
\[ (4) \]

where \[ \alpha_1 = m_C/m_{C_{\infty}}; \quad \alpha_2 = m_H/m_{H_{\infty}} \]
\[ K_1' = M_C/M_A; \quad K_2' = M_H/M_F \]
\[ K_1 = m_{A_0}K_1'; \quad K_2 = m_{F_0}K_2' \]
\[ m_{C_{\infty}} = m_{A_0}M_C/M_A; \quad m_{H_{\infty}} = m_{F_0}M_H/M_F \]
\[ m_{A_0} + m_{F_0} = m_0. \]

The meanings of the symbols used in the above formulas are as follows:

- \( m_0 = \) initial weight of sample
- \( m_c, m_E \) and \( m_H \) = weights of gaseous compounds \( C, E \) and \( H \) evolved during decomposition in time \( t \)
- \( m_{C_{\infty}}, m_{E_{\infty}} \) and \( m_{H_{\infty}} \) = weights of compounds \( C, E \) and \( H \) which correspond to their complete formation
- \( m_{A_0} \) and \( m_{F_0} \) = weights of compounds \( A \) and \( F \) before decomposition
- \( M_A, M_C, M_E, M_F \) and \( M_H \) = molecular weights of the respective compounds
- \( \alpha_1 \) and \( \alpha_2 \) = conversion degrees in the individual decomposition stages.

On substituting the values \( \alpha_1 = 1 \) and \( \alpha_2 = 0 \) into Eqs (3) and (4), we obtain in both cases

\[ y_1 = K_1 \]  
\[ (5) \]

Thus, constant \( K_1 \) accounts for the total weight loss in the 1st reaction stage.

By introducing the values \( \alpha_1 = 1 \) and \( \alpha_2 = 1 \) into Eqs (3) and (4), we receive

\[ y_{1,II} = K_1 + K_2 \]  
\[ (6) \]

Constant \( K_2 \) can be found from Eqs. (5) and (6) as the weight loss of the sample in the 2nd decomposition stage. From analogous reasoning for the three-stage