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THE RELIABILITY OF KINETIC DATA BY THERMAL ANALYSIS FROM THE ASPECT OF TECHNOLOGICAL APPLICATION

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ABSTRACT

New evaluation method for complex, overlapping thermogravimetric processes is described. The E^* vs. (1-x) or E^* vs. 1/T functions are suitable for the quantitative qualification of different industrial products e.g. motor oils etc. and to look for the effects on their quality.

INTRODUCTION

The sharp debate about the kinetic evaluation of thermoanalytical data indicates that this problem has not been solved, yet. Without disputing the wellfoundedness of the different efforts, we can classify the opinions and efforts concerning the description of the measured data as follows:

- forming and choosing differential equations suitable to the description of the processes /e.g. 1,2/.
- efforts to solve the problems by the improving of the messurement conditions,
- criticism of the Arrhenius-type equations, restriction of their use /e.g.3/, even "prohibition" of them /4/,
- criticism of the kinetic evaluability of the measurements/5/,
- analysis of the problems as a basis of the potential solution /e.g. 3,6/.

These manifolded efforts mutually overlap each other and it can be stated that the formal kinetic description of some overlapping thermal processes is almost hopless, if one aims a faultless description in the classical sense. In such a form the problem arises especially in case of analysis and development of industrial products of complicated composition. In this case, the quantitative description of thermal processes has a great significance even if it is entirely formal, but it makes possible the

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comparison of substances or the separation of effects originating from the properties of the substances or from the measuring conditions. The solution of this problem is a completion of the abov: mentioned efforts as a subject of this discussion.

RESULTS AND DISCUSSION

Considering the experience of the thermoanalytical measurements and of their kinetic evaluation, we found that for the evaluation of overlapping processes the recommended differential equations are:

- practically equivalent, if we consider the correlation coefficient of the description,
- the correlation coefficient of the description is high even in the case of the simplest usual equation,
- the suggested differential equations function like polynoms, if the data calculated by various equations show the kinetic compensation effect,
- relationships exist among the kinetic constants generally, it means that not only between the logarithm of preexponential factor and the activation energy /kinetic compensation effect/, but among these and the reaction order or orders, too,
- the great majority of the thermal processes are so complicated, that their decomposition mechanism cannot be concluded only from their kinetic constants /7,8/.

On this basis for the formal description of multiple overlapping processes, such as the thermal decomposition of polymers, motor oils or hydrated cements etc. we started from the following well-known differential equation.

$$-dx/dT = A \exp\left(-E/RT\right) \left(1-x\right)^n \qquad (1)$$

Considering the "A" and "n" equal to 1, the value of "E" can describe the complex processes:

$$E_i^{*} = E_i/R = T_i \left[\ln\left(1-x\right)_i - \ln\left(-dx/dT\right)_i\right] \qquad (2)$$

where:

T_i is the measured temperature in K,

$\left(1-x\right)_i$ is the reaction coordinate calculated from the TG curve,

$\left(-dx/dT\right)_i$ is the rate of weight change of the process.

The equation 2 maintains the structure of the original differential equation, but it uses only measured data without any arbitrary supposition concerning with the kinetics.

In case of relatively simple processes /e.g. decomposition of $CaCO_3$/ a possibility occurs for quantitative characterization of the effects of measuring conditions by transforming the E^{*} data with suitable calculated "A" and "n" values for comparison /7/.

In case of multiple overlapping processes e.g. the thermal decomposition of motor oils, when different physical processes superimpose on the chemical processes originated from the complicated chemical composition, the differences in the E^{*} vs. $(1-x)$ or in the E^{*} vs. $1/T$ functions are suitable for the quantitative comparison of different examined substances. To look for the different effects on the quality of the examined substances is also possible by these functions.

Figure 1 shows the E^{*} vs. $(1-x)$ and the E^{*} vs. $1/T$ functions of a commercial motor oil. The measurement was made with Derivatograph /9/ using 200 mg sample and 5 K/min heating rate.

Figure 2 shows the average values of the deviations from the mean as a function of the reaction coordinate interval from the results of repeated measurements with the same oil. Considering that the values of E^{*} is greater than 3000 in the case of motor oils generally, the reproducibility of the method is good enough. The deviation from the mean is smaller than 1 % even in the case of 3 °C generated error. The relation between the error and the reaction coordinate shows that under the above measuring conditions, it is advisable to neglect only the first and the last 10 % of the weight loss at the evaluation of the results.

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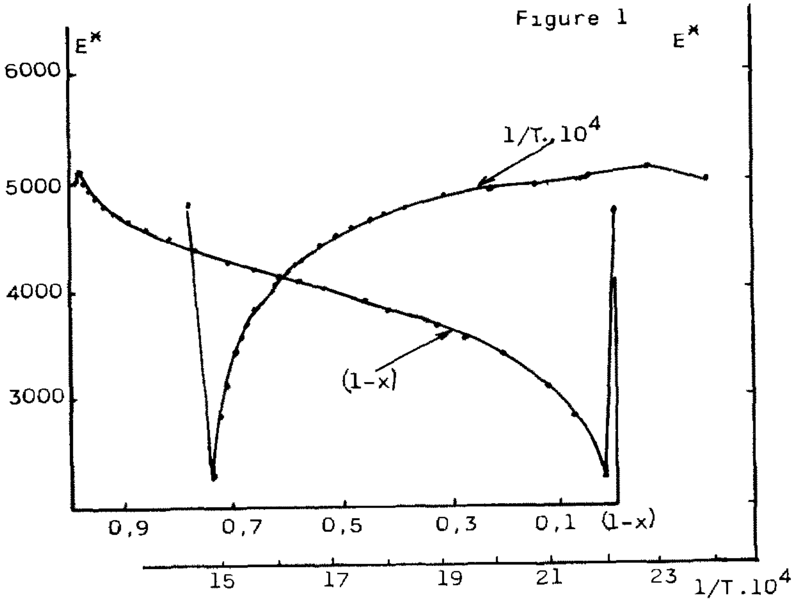
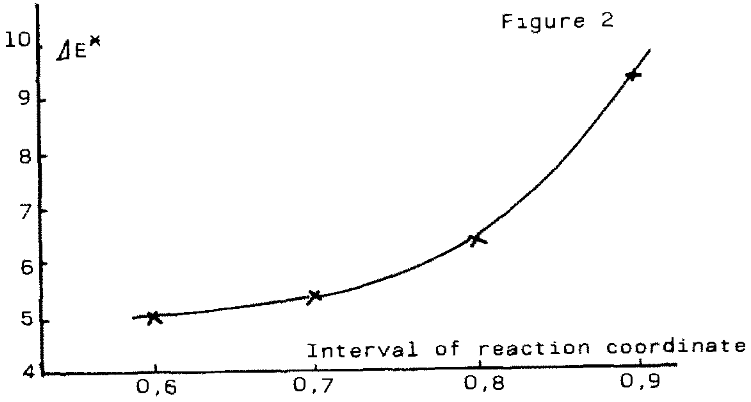
Figure 1



E^* vs. (1-x) and E^* vs. 1/T functions of a commercial motor oil

Figure 2



Correlation between the error of measurements and the interval of reaction coordinate