INVESTIGATION ABOUT METHODS OF QUANTITATIVE EVALUATION OF DTA CURVES

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The investigation gives a comparison of the best-known kinetic evaluation methods for DTA curves. With regard to accuracy and error-compensation, the methods of Borchardt and Daniels, Coats and Redfern and Satava and Škvara in particular are to be recommended if simple irreversible reactions are to be evaluated on the basis of homogeneous kinetics. The complete exponential integral method is described which totally eliminates the approximative character of the practical procedure of Coats and Redfern. Hence, it becomes theoretically exact again.

In an estimation of the accuracies and sensitivities of well-known methods of evaluating differential thermal analysis (DTA) or differential thermogravimetric (DTG) curves, it is necessary to compare these procedures using defined curve shapes. It is obvious to apply synthesized model curves, as will be demonstrated very precisely under defined premises by means of a computer. Other subjects of comparison, such as selected experimental DTA or DTG and EGA curves, respectively, are influenced by unknown error sources a priori. Such effects lead to inadmissible generalizations, as in the testing of some evaluation procedures by Chen [1].

The present investigation starts from a homogeneous irreversible first-order model reaction, produced using the computing program DTA-t for the following parameters, including the Arrhenius equation:

\[
\begin{align*}
H_R &= 40 \text{ kcal mole}^{-1} \\
E &= 20 \text{ kcal mole}^{-1} \\
k_0 &= 10^{12} \text{ min}^{-1} \\
c &= 0.1 \text{ mole l}^{-1} \\
q &= 3.75 \text{ deg min}^{-1} \\
V &= 0.005 \text{ l} \\
C_p &= 5.714 \text{ cal deg}^{-1} \\
K &= 4.0 \text{ cal deg}^{-1} \text{ min}^{-1} \\
\end{align*}
\]

\[
\begin{align*}
\frac{dx}{dt} &= \frac{c}{KA} \left[ C_p \left( \frac{dT}{dt} + KT \right) \right], \text{ with } A = \int_{0}^{\infty} AT \, dt \\
&= k_0 \exp\left(-\frac{E}{RT}(c - x)^n\right)
\end{align*}
\]

Figure 1 shows the theoretical DTA curve, as well as one with incidental errors; another curve with larger errors will be presented later. The mean error in \(\Delta T\) amounts to 8 and 14 percent, respectively. The theoretical curve was calculated.
down to 0.1 percent of $\Delta T_{\text{max}}$, but values down to 10 percent of $\Delta T_{\text{max}}$ were generally involved in the comparisons.

For the comparisons eight well-known methods were employed. The method of Kissinger [2] was included, although it needed more than two DTA curves at different heating rates $q$, which makes unclear the consideration of error-affected curves. Figure 2 illustrates six exact model curves with variation of $q$ from 0.5 to 10 degree min$^{-1}$. Relative large deviations from the linearity of Eq. (3) are visible even in the region of low temperatures of the DTA maximum, $T_m$:

$$\frac{d \log q/T_m^2}{d(1/T_m)} = -\frac{E}{2.3 R}$$

(3)

Putting the temperature of the maximum of the reaction rate $T_{m\text{r}}$ equal to the temperature of the DTA maximum, $T_m$, is still not allowed for $q = 0.5$ deg min$^{-1}$.