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MORE PRECISE METHODS OF KINETIC ELECTRONIC COMPUTER TREATMENT OF GRAVIMETRIC CURVES

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ABSTRACT

The authors propose a procedure of more precise computed treatment of thermal analysis curves following the rule of formal kinetics proceeding from the assumption that the DTG curve is an exact differential of the investigated mass sample time and temperature differentiated. The authors give their results obtained by using the proposed technique and compare them with the classical methods of isothermic kinetics.

TECHNIGUE

Mass of any system compoment is directly connected with its chemical potential, and its mass change ought to be exact differential of independent variables determining the state of the system. Therefore DTG curve with temperature (T) and process duration (τ) change represents the total mass derivative of sample (M) according to the variables

$$\frac{dM}{d\tau}=\frac{\partial M}{\partial \tau}+\frac{\partial M}{\partial T}\cdot\frac{dT}{d\tau} \quad . \qquad (1)$$

Meanwhile the mass action law is valid only to mass partial time derivative

$$\frac{\partial M}{\partial \tau}=A_0\cdot S\cdot C^{n}\cdot exp(-\frac{E}{RT}) \qquad (2)$$

(A_0 - preexponential factor, S - surface reaction area, C - gaseous reagent concentration, n - process order, E - activation energy, R - gas constant, T - absolute temperature), in this connection DTG curve'application for direct data processing as formal kinetic process rate appears to be mathematically incorrect.

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Having in mind equation (1) it is necessary at first to find general expression of sample mass dependence on temperature and process duration for subsequent partial derivative determination $\frac{\partial M}{\partial \tau}$ in kinetic analysis. Such general expression is provided by regressive analysis of computer processed data array obtained from thermogravimetry and temperature curves. Then polynomial two factor dependence of the sample mass (or degree of reaction realization α) will be

$$M = a_0 + a_1 T + a_2 \tau + a_3 T\tau + a_4 T^2 + a_5 \tau^2 + a_6 T^2 \tau + \ldots \quad . \quad (3)$$

One more parameter (e.g. concentration) if it is needed may be taken into account too. Then temperature and process duration dependence of formal-kinetic process velocity will be defined by partial derivative

$$\frac{\partial M}{\partial \tau} = a_2 + a_3 T + 2 a_5 \tau + a_6 T^2 + \ldots \quad . \qquad (4)$$

For activation energy calculation according to (2) constant magnitude of surface reaction (S) at different T is necessary, and it is usually kept at equal α under identical experimental conditions. So, process velocity equation expressed in terms of T and M (α) is the most convenient one for the analysis. Such an equation is simply obtained by substitution $\tau = f\ (T,M)$ into (4), derived from (3), or deduced by regressive method using the same initial data array

$$\tau = b_0 + b_1 M + b_2 T + b_3 TM + b_4 T^2 + b_5 M^2 + \ldots \quad . \qquad (5)$$

Substitution of (5) into (4) gives the desired dependence

$$\frac{\partial M}{\partial \tau} = a_2 + a_3 T + 2 a_5 (b_0 + b_1 M + b_2 T + b_3 TM + b_4 T^2 + \ldots) + a_6 T^2 + \ldots \quad . (6)$$

From this equation for any given M (or α) a set of velocities for corresponding temperature set is obtained followed by activation energy calculation according to Arrhenius -type equation. Thermal analysis at different gaseous component concentratinos gives such initial data, from which it is possible using the above method to obtain $M = f_1(\tau, T, C)$, $\tau = f_2\ (M\ T, C)$ and $\frac{\partial M}{\partial \tau} = f_3(M, T, C)$ dependences, permitting the process order n in $\ln \frac{\partial M}{\partial \tau} - \ln C$ coordinates be derived.

Since kinetic behaviour possesses as a rule of exponential character it is advisable to assume two-factor dependences of the degree of reaction realization as

$$\alpha = 1 - \exp\left[-A\tau^{m}\exp\left(-\frac{B}{T}\right)\right], \qquad (7)$$

where A and B are constants. In the case after taking log-log of (7) DTG, T and TG data may be approximated to the equation (7) by least- squares procedure and A, B, m be obtained. After differentiation of (7) followed by $\tau = f\ (\alpha, T)$ substitution from (7) into differential equation velocity expression

$$\frac{\partial\alpha}{\partial\tau} = Am\left[-\frac{\ln(1-\alpha)}{A}\right]^{\frac{m-1}{m}}\exp\left[\ln(1-\alpha) - \frac{B}{Tm}\right], \qquad (8)$$

may be obtained, from which just as from (6) kinetic process parameters may be derived (in a number of cases, e.g. at dissociation B coefficient is identified with $\frac{E}{R}$, and m is topokinetic order). Exponential variant is simpler for solution as equation (7) is linearized with comparative ease and is identified by a desktop calculators.

RESULTS AND DISCUSSION

Investigation of calcium oxalate ($CaC_2O_4 \cdot H_2O$) dehydration and lump coke (5 - 20 mm) drying by F.Paulik, J.Paulik, I.Erdey derivatograph in air atmosphere with heating rates in the range of 3,8 - 6,2 K/min (samples 1,99 - 2,00 g) was performed to test the proposed method of derivatogram kinetic processing. The obtained thermal analysis curves were processed by a special electronic computer (Minsk - 32) program, based on least-squares procedure. As a result of computer processing the coefficients of equation (7) were obtained for coke drying

$$\alpha = 1 - \exp\left[-2496\,\tau^{0,8868}\exp\left(-\frac{4322}{T}\right)\right] \qquad (9)$$

with significant correlation R = 0,950 and $CaC_2O_4 \cdot H_2O$ dehydration

$$\alpha = 1 - \exp\left[-1,324 \cdot 10^{8}\,\tau^{0,9223}\exp\left(-\frac{10620}{T}\right)\right] \qquad (10)$$

with significant correlation R=0,986.

Activation energy of coke drying from (9) equals to 35,74kj/mol and is in accord with isothermal experiment results (36,80kj/mol). Topokinetic process order approximated to unity (0,89). For oxalate calcium dehydration E=84,44 kj/mol, m=0,92 are in good agreement with isothermal experiment results too, carried out for comparison.

Thus, it can be ascertained, that the method provides reliable results, the accuracy of which may be additionally raised both by initial data array increase and degital recording of derivatographic data and direct processing them by an electronic computer.