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"IGNITION" CRITERIA IN DIFFERENTIAL THERMAL ANALYSIS

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The "Ignition" criteria taken from the theory of combustion are suggested for the determination of various kinetic characteristics with the thermophysical parameters depending upon the temperature.

The result of application of the "Ignition" criteria to determine the activation energy of magnesite are presented.

It is shown that on taking into account a linear relationship between the temperature and the heat capacity and the heat conductions of magnesite and the reference material E proves to be much lower than the value of activation energy obtained with the assumption that the thermophysical parameters do not depend on it.

A close kinetic study of decomposition processes by DTA and DSC methods under scanning conditions over a wide range of temperatures shows that the problem can commonly be regarded as a system of three non-linear differential equations of the following type:

$$C_m(T_m)\frac{\partial T_m}{\partial t} = \frac{\partial}{\partial x}\left[\lambda_m(T_m)\frac{\partial T_m}{\partial x}\right] + \frac{K}{x}\lambda_m(T_m)\frac{\partial T_m}{\partial x} \pm H(m-1)\frac{d\alpha}{dt}; \tag{1}$$

$$\frac{d\alpha}{dt} = \phi(\alpha)Z\exp\left(-\frac{E}{KT_2}\right); \tag{2}$$

$$\lambda_m(T_m)\left.\frac{\partial T_m}{\partial x}\right|_{x=\Delta} = Q_m; \quad \left.\frac{\partial T_m}{\partial x}\right|_{x=0} = 0;$$

$$m = 1, 2$$

where T is the temperature, α is the degree of conversion, and C_m and λ_m are the heat capacity and heat conduction of the sample ($m = 2$) and the reference ($m = 1$), respectively. $\phi(\alpha)$ is the function determining the reaction order, H is the calorific effect of the reaction, Z is the frequency factor, and Q_m is the heat flow warming up the cells. Δ is half the layer thickness [for substance or solutions] in the case of a plane cell ($k = 0$) or a radius for spherical ($k = 2$) or cylindrical ($k = 1$) elements.

The analytical solution of this problem does not seem possible at present. In this connection the search for and application of different methods of approach simplifying the determination of the main kinetic parameters are a matter of great interest. One approach is the mode of introduction of the "Ignition" criteria [1]. This method has been successfully used in combustion physics.

According to the criteria the conversion process becomes noticeable when the heat absorption or desorption power is equal to the heat power of external sources or sinks.

With variation of the scanning speed, the activation energy and various complex values including thermophysical parameters can be determined from experimental data for the temperature T (or time) corresponding to equality of heat flows, by the substitution of this value into the equation for heat balance

$$Hz \int_0^{\Delta} \left[\exp\left(- \frac{E}{KT_i(x)} \right) - \exp\left(- \frac{E}{KT_0} \right) \right] x^K dx = q_s(T_i); \tag{3}$$

The introduction of the "Ignition" criteria has the result that the equation for heat conduction can be solved without taking the conversion process into consideration. In other words the system of three equations (1) and (2) is reduced to one equation, provided that $m = 1$.

Thus, the problem is considerably simplified. In particular, if λ and C do not depend on T, the equations for heat conduction and boundary conditions are linear and can therefore easily be integrated.

The symbol q_r denotes the heat power absorbed or desorbed referred to the volume of the medium during the conversion process.

The symbols q_1 and q_2 mean the heat powers of all sources per unit of medium volume in reference and sample cells, respectively. Thus, the relationship between q_1, and q_2 is expressed as follows:

$$q_2 = q_1 \pm q_r$$

As far as the usual Differential Thermal Analysis is concerned, it is impossible to compare heat flows from external sources and the flow which accompanies the conversion process in a separate cell, because as a rule

$$q_r \ll q_1$$

But suppose there is a DTA curve corresponding to the temperature of a third hypothetical medium warmed up by the differential heat flow $q_2 - q_1$. In such an interpretation application of the "Ignition" criteria seems to be quite reasonable.

In the DTA apparatus $| q_2 - q_1 | - | q_r |$ is always equal to zero, and therefore $\delta T = T_1 - T_2$ is always unequal to zero, as the thermophysical properties of the reference and the sample are different. Assuming that $\delta T = 0$, we have $| q_2 - - q_1 | - | q_r | \neq 0$. This means that to maintain the baseline in our introduced hypothetical medium a heat energy sink with heat power $| q_2 - q_1 | - | q_r |$ must be involved in the system.

Taking this into account, the equation of the "Ignition" criteria for DTA is:

$$\exp\left(-\frac{E}{KT_i}\right| - \exp\left(-\frac{E}{KT_0}\right| = |0 - \{|q_2 - q_1| - |q_r|\}(Hz)^{-1} =$$

$$= ||q_2(T_i)| - |q_1(T_i)||(Hz)^{-1}; \tag{4}$$

where $q_1(T_i)$ and $q_2(T_i)$ are the specific heat powers at the moment when $T_1 = T_2 = T_i$. They should be fed into the reference cell and the sample cell, respectively, so that at thermocouple locations $T_1(t) \equiv T_2(t)$.

The "Ignition" criteria are applied to the analysis of DTA curves for magnesite [2] for determination of the activation energy. We have studied two variants.

1) λ_m and C_m are assumed to be constant.

2) λ_m and C_m are in linear relationship with T_m.

In the first case Eq. (4) will be as follows:

$$\frac{\phi(C_1 - C_2)}{Hz} = \exp\left(-\frac{E}{KT_i}\right| - \exp\left(-\frac{E}{KT_0}\right|; \tag{5}$$

where ϕ is the heating rate.

Calculation of the value E was made in two ways: including T_0 and ignoring it. In the first case the equation for E will be as follows:

$$E = \left|\frac{KT_{i1}T_{i3}}{T_{i3} - T_{i1}}\right| \ln \left|\frac{(\phi_3 - \phi_1)\,T_{i1}(T_{i2} - T_{i3})}{(\phi_3 - \phi_2)\,T_{i2}(T_{i3} - T_{i1})}\right|; \tag{6}$$

In the second case:

$$E = \left|\frac{KT_{i1}T_{i3}}{T_{i3} - T_{i1}}\right| \ln \left|\frac{\phi_3 T_{i3}(T_{i1} - T_0)}{\phi_1 T_{i1}(T_{i3} - T_0)}\right|; \tag{7}$$

Since the dynamic components of specific heat and heat conduction are usually very small, the "ignition" moment T_{iK} may be specified as a temperature value at which the DTA resultant curve has a slope twice as high as that of the baseline.

After calculation of Eq. (2) for three heating rates $\phi_1 = 1.75\ \frac{\text{deg}}{\text{min}}$, $\phi_2 = 3.46\ \frac{\text{deg}}{\text{min}}$ and $\phi_3 = 5.56\ \frac{\text{deg}}{\text{min}}$ we obtained the following values:

$$T_{i1} = 644 \cdot 1\ \text{K}; \quad T_{i2} = 655\ \text{K}; \quad T_{i3} = 653\ \text{K} \quad \text{at} \quad T_0 = 623\ \text{K}.$$

In accordance with these data, E from Eq. (6) is $86\ \frac{\text{kcal}}{\text{mole}}$ and E from Eq. (7) is $77.5\ \frac{\text{kcal}}{\text{mole}}$.

The activation energy calculated with the "Ignition" criteria proves to be in excess of 30%. This was established and illustrated by a number of examples [1].

Taking into account this permanent correction, we obtain for the average E approximately 62.8 $\frac{\text{kcal}}{\text{mole}}$, which correlates well with the data presented in [2].

Some difference in the values of energy obtained from various equations can be explained by the fact that in our calculation we had to use the value 3.46 $\frac{\text{deg}}{\text{min}}$ for the heating rate, which seems to be doubtful [2].

In case 2

$$\lambda_m = \lambda_{0m} + \lambda_{m\sim}(T - T_0)$$

$$C_m = C_{0m} + C_{m\sim}(T - T_0)$$

The solution of the heat conduction equation for this case is presented in [3]. Since in experiment [2] measuring thermocouples were placed in the center of the cells, for corresponding temperatures we obtain the two following equations:

$$\frac{d\theta_1}{dF_0} = \frac{Q_1}{(1 + C_{1\sim}\theta)\left[\frac{1}{3} - \frac{Q_1\lambda_{1\sim}}{10(1 + \lambda_{1\sim}\theta_1)^2}\right]}; \tag{8}$$

$$\frac{d\theta_2}{dF_0} = \left\{\frac{Q_2\xi}{1 + C_{2\sim}\theta} - \frac{1}{10(1 + \lambda_{2\sim}\theta_2)} \cdot \frac{dQ_2}{dF_0}\right\}\left\{\frac{1}{3} - \frac{Q_2\lambda_{2\sim}}{10(1 + \lambda_{2\sim}\theta_2)^2}\right\}; \tag{9}$$

Here F_0 is the Fourier number, and $\xi = \frac{a_{02}}{a_{01}}$, a_{01}, a_{02}, $c_{1\sim}$, $c_{2\sim}$, $\lambda_{1\sim}$, $\lambda_{2\sim}$ are temperature conduction, and dimensionless variables of specific heats and heat conductions of the reference and the sample cells, respectively.

θ_i and Q_i are dimensionless temperatures in the center and the heat flow densities on the surface of the reference cell and the sample cell.

From Eqs (8) and (9) we can easily find the relationship where Q_1 and Q_2 may be used so that $\theta_1(F_0) \equiv \theta_2(F_0)$

$$\frac{dQ_2}{d\theta} = \frac{10\,Q_2\xi(1 + \lambda_{2\sim}\theta)(1 + C_{1\sim}\theta)}{(1 + C_{2\sim}\theta)Q_1} \cdot \left\{\frac{1}{3} - \frac{Q_1\lambda_{1\sim}}{10(1 + \lambda_{1\sim}\theta)^2}\right\} - \\ - \frac{10(1 + \lambda_{2\sim}\theta)}{3} + \frac{Q_2\lambda_{2\sim}}{1 + \lambda_{2\sim}\theta}. \tag{10}$$

As a rule the cells in the DTA apparatus are small, and therefore the difference between the average specific heat power $\frac{3\,Q_m}{\Delta}$ and the heat power q_m in the center may be ignored.

As a result, from Eq. (10) we obtain for the differential heat power δq in the linear approximation:

$$\delta q = \gamma + \beta\phi(T - T_0) = \gamma + \beta\phi\delta T \tag{11}$$

where γ and β are certain given functions of thermophysical parameters for the reference and the sample, H and Z.

From Eqs (11) and (4), if the data for the three heating rates ϕ_K $(k = 1, 2, 3)$ are available, we have

$$E = K\left|\frac{T_{i1}T_{i3}}{T_{i3} - T_{i1}}\right| \ln \left|\frac{(\phi_3\delta T_{i3} - \phi_1\delta T_{i1})\, T_{i1}(T_{i2} - T_{i3})}{(\phi_3\delta T_{i3} - \phi_2\delta T_{i2})\, T_{i2}(T_{i3} - T_{i1})}\right| \approx 66.2\,\frac{\text{kcal}}{\text{mole}}\,; \qquad (12)$$

and, taking into account the correction, we obtain: $E = 51\,\frac{\text{kcal}}{\text{mole}}$.

Thus, with the linear relationship between thermophysical parameters and temperature for magnesite, the value of the activation energy proves to be noticeably lower in comparison with that obtained with the assumption that λ and C are constant.

To summarize the above it may be said that if the "Ignition" criteria are applied in Differential Thermal Analyses, then:

1. In the case of constant thermophysical parameters the analysis of a three non-linear equation system may be replaced by the integration of one linear equation, the exact solution of which is known. This is just one typical situation when the "Ignition" criteria may be an express method of evaluating the activation energy in a quick and simple way.
2. In the case when the parameters depend on temperature, the system of three non-linear equations, the solution of which is considered to be impossible, reduces to one non-linear equation without a source, the approximate integration of which presents no difficulties.
3. The results do not depend upon such an important characteristic as the heat resistance of the instrument, because in the criteria the temperature of "ignition" is determined by the curve slope ratio $\delta T(T)$, both taking into account the conversion process and without it, but not by the value of the slope itself.

References

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Résumé — On propose une méthode pour déterminer les caractérististiques cinétiques des phénomènes d'ignition en faisant appel à la théorie de la combustion et en tenant compte de l'influence de la température sur les paramètres thermophysiques.

On applique la méthode à la détermination de l'énergie d'activation de la magnésite. On montre qu'en tenant compte d'une relation linéaire entre la chaleur spécifique et la conductibilité thermique de la magnésite et de la substance de référence d'une part, ainsi que de la température d'autre part, la valeur de l'énergie d'activation E est beaucoup plus faible que celle que l'on obtient en supposant que les paramètres thermophysiques ne dépendent pas de la température.

ZUSAMMENFASSUNG — Die aus der Verbrennungstheorie abgeleiteten »Entzündungs« Kriterien werden zur Bestimmung verschiedener kinetischer Kennzeichen mit von der Temperatur abhängenden thermophysikalischen Parametern vorgeschlagen. Die Ergebnisse der Anwendung der »Entzündungs« Kriterien zur Bestimmung des Aktivierungsenergiewertes von Magnesit werden vorgeführt.

Den linearen Zusammenhang zwischen Wärmekapazität und Wärmeleitfähigkeit, sowie die Referenz einerseits und die Temperatur anderseits in Betracht genommen, wird gezeigt, daß E viel niedriger ist als der Aktivierungsenergiewert, erhalten unter der Annahme, daß die thermophysikalischen Parameter nicht von der Temperatur abhängig sind.

Резюме — Для определения различных кинетических характеристик в случае зависящих от температуры теплофизических параметров предлагается использовать критерий «зажигания», заимствованный из теории горения. Приводятся результаты применения критерия для определения энергии активации магнезита. Показывается, что при учёте линейной зависимости теплопроводности и теплоёмкости магнезита и эталона от температуры значение Е оказывается заметно ниже энергии активации, найденной в предположении независимости теплофизических параметров от T.