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REDUCED-TIME PLOTS IN THE THERMAL DECOMPOSITION OF SOLIDS, PAST, PRESENT AND FUTURE

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ABSTRACT

The problem of reduced-time plots is examined here in its development in topochemistry. The position of the points in relation to the temperature at constant α on the $\alpha - t_r$ curve of a non-isokinetic process (the thermal decomposition of CoOOH) has been investigated. It has been found that t_r is dependent on temperature. This is ascribed, on the one hand, to the presence of an initial non-isothermal period of the process and, on the other, to its non-isokinetic character.

THE PROBLEM

In isothermal topochemical kinetics the course of a reaction is usually expressed by monitoring the degree of its passage, α, with time at constant temperature. As a result, a series of kinetic (α–t) curves, describing the course of the process in a certain temperature range, is obtained (Fig. 1). If, however, the time is plotted on the abscissa not in generally accepted but in relative units, connected with the passage of the very process (say, the ratio of the time, t, at a certain moment of the process to the time $t_{0.5}$ of its 50% passage), then its course in that temperature range is described in principle only by a kinetic curve, the so-called reduced-time plot or α–t_r curve (Fig. 2). According to current knowledge, the following features are ascribed to it.

(1) It expresses the course of the process only by a single curve over the whole temperature range of its passage instead of by a series of curves differing in temperature. Consequently, this form may be considered as a step toward the intensification of the isothermal method and its equalization in this respect with the polythermal method.

(2) As a dimensionless curve, whose coordinates change within the same limits, regardless of temperature, it gives a good idea about the real geometric shape of the chart of the process, from which general information about its course can be obtained, as well as the possibility of comparing it with the theoretical α–t_r curve plotted by means of a mathematical equation of the correponding model.

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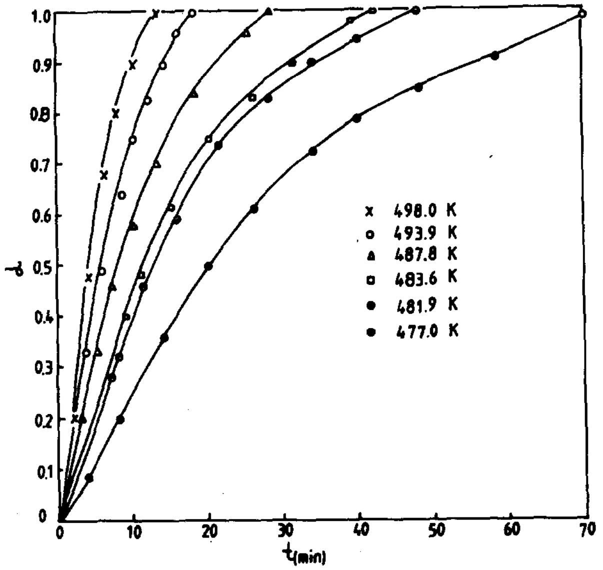

Fig. 1. $\alpha - t$ curves for the decomposition of hexahydro-1,3,5-trinitro-*s*-triazine (RDX) [1].

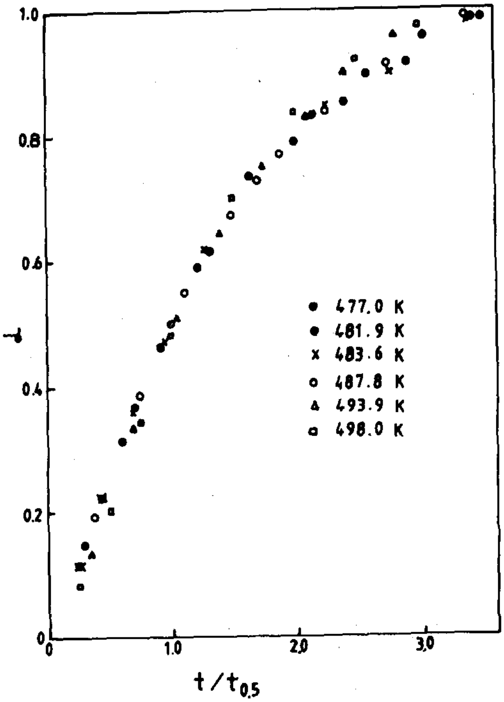

Fig. 2. $\alpha - t_r$ curve for the decomposition of RDX [1].

(3) Since the reduced-time plot in the case examined also records the effect of temperature, it may be assumed to reflect possible changes in the mechanism of the process with a change in temperature, i.e., provide information on whether or not the process in the temperature range examined is isokinetic in character. This would seem to be the most specific and foremost feature of the α–t_r curve, reflecting its greater sensitivity than the classical α–t curve to the particularities of the process.

The concept of isokinetic character of a process [2] expresses its passage within a certain assumed kinetic model. This means that some of the kinetic characteristics of the process are constant: the kinetic equation along which it proceeds and, especially, the value of its activation energy within the examined range. When these change, the process is seen to follow a non-isokinetic course.

HISTORY

According to Delmon [3], the reduced-time coordinates were proposed way back in 1939 [4], but it is only in the '60s that they began to be used, mainly on the processes of thermal decomposition of solids. In the '50s the non-isothermal gravimetric curve (TG) was introduced in thermal analysis, whose main advantage over isothermal gravimetric curves is the possibility of encompassing, with one curve, the process over its entire temperature range. It is probably this which has prompted scientists, albeit subconsciously, to seek a solution with respect to the isothermal method as well. At first this idea was realized by means of the standard curve method [5–9], in which an α–t curve from a given series is picked as the master curve. The other curves are then superimposed on it by a suitable change in the t scale when selecting a point common to all curves, say for $\alpha = 0.5$. The reduced plot thus obtained, although equivalent in results to the subsequently introduced α–t_r curve [1,3,10–13], is not completely dimensionless, because t is again expressed in the generally accepted time units. On the other hand, it can hardly be examined on a general mathematical basis.

In 1966 Sharp et al. [10] proposed a simple and universal method for converting the kinetic equation from its conventional into a reduced-time form, through which it is characterized not only analytically but also by the constant shape of its α–t_r chart. Thus, reduced-time curves obtained a theoretical basis, which extended their application to topochemistry.

As soon as reduced plots made their appearance, attempts were made to interpret them with a view to the mechanism of the respective process. Thus, for instance, the grouping of points around the curve (not plotted on the drawing) in Fig. 2 was taken to be an indication that the process in the region investigated is isokinetic in character. This chart, as well as its predecessors, suffers from two shortcomings as regards the possibility of analysing the position of the points. First, they are plotted while simultaneously varying α and t_r for different temperatures. Second, the scale of the abscissa is too rough, five times more so than that of α. These conditions are naturally not conducive to a juxtaposition of the disposition of the points at different temperatures.

In 1980 Dollimore et al. [13] proposed a variant of the α–t_r curve (Fig. 3), in which the above shortcomings have been removed. The comparison of t_r at different temperatures is effected here at a constant α value; moreover, the scale of t_r is only twice as rough as that of α, which may be said to be an optimal ratio. Now, however, a considerable scattering of the points on the α–t_r curve can be observed. This disturbed the authors [13], so that they claimed an "only approximate" isokinetic character for the process.

OUR INVESTIGATIONS

The position of the points at different temperatures is not shown in Fig. 3, nor has an attempt been made to explain the aforementioned scattering, which does not seem to be due to random errors. Proceeding from there, we set ourselves the following two tasks:

(1) to trace the position of the separate points in relation to temperature for an α–t_r curve plotted by the model in Fig. 3, as well as possibly to explain their scattering;

(2) the α–t_r curves have been used so far chiefly in support of the isokinetic character of a certain process. We shall examine the case from its inverse side, setting the question: how will a reduced-time plot of a process which is non-isokinetic in a certain temperature range look?

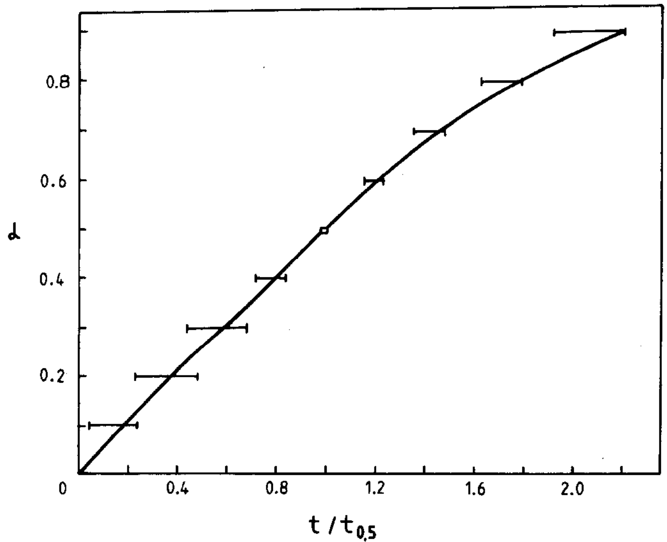

Fig. 3. α–t_r curve for the decomposition of $ZnCO_3 \cdot 2ZnO \cdot 2H_2O$ [13].

Such a process is, for instance, the thermal decomposition of CoOOH, which proceeds according to the equation

$$12\mathrm{CoOOH} \rightarrow 4\mathrm{Co_3O_4} + 6\mathrm{H_2O} + \mathrm{O_2} \tag{1}$$

and is quite familiar [14,15]. Our investigations reveal that at a random temperature T between 260 and 310°C it is subject to the kinetic equation

$$1-(1-\alpha)^{1/2} = k_T t \tag{2}$$

where α is the extent of decomposition, k_T the rate constant, and t the time, expressed in conventional units. At about 280°C the process changes the value of the activation energy from $E_1 = 145.5$ kJ mol^{-1} to $E_2 = 79.1$ kJ mol^{-1} (Fig. 4), which suggests a non-isokinetic character, as also confirmed by other authors [16]. Consequently, the changes in the reaction mechanism in this case do not affect the main kinetic model: the contracting disc model, whose equation remains in force over the entire temperature range. Any change in the Arrhenius plot should not be considered as necessarily involving a change in the corresponding rate law [16]. There are cases [17–23], when changes in the mechanism affect its characteristics without this necessarily leading to a change in the kinetic equation of the process, i.e., the changes occur within the framework of the basic kinetic model used.

According to ref. 10, when substituting $\alpha = 0.7$ and $t = t_{0.7}$ in eqn. (2), we get

$$0.4523 = k_T t_{0.7} \tag{3}$$

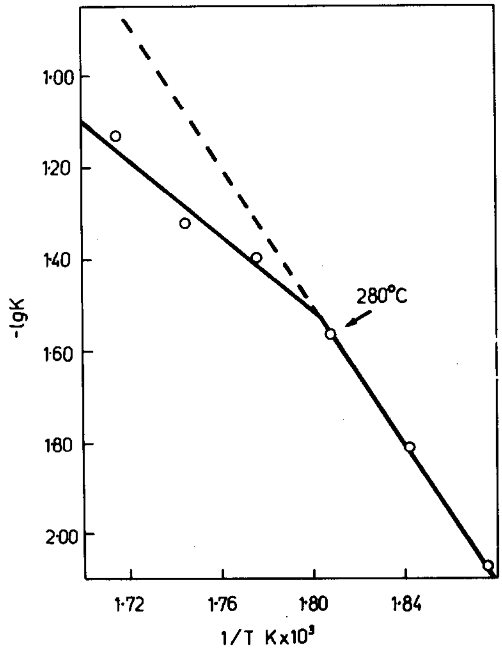

Fig. 4. Arrhenius plot for reaction (1) [14].

and, combining (2) and (3), we get

$$1-(1-\alpha)^{1/2}=0.4523t_r \qquad (4)$$

where $t_r = t/t_{0.7}$ is the reduced time. Equation (4) is the reduced-time form of eqn. (2). Since t and $t_{0.7}$ depend on k_T, their ratio, or t_r, will be independent of k_T only if the latter undergoes no changes at the temperature T, i.e., if eqn. (2) is valid for the entire decomposition process. In that case eqn. (4) becomes universal, because it depends neither on the chemical nature of the process nor on the temperature. It requires only that all topochemical processes subject to eqn. (2) be described by one and the same α–t_r curve.

The experimental points for the α–t_r curve of reaction (1) are shown in Fig. 5. Two particularities can be observed in the disposition of the points in relation to the temperature: (1) the t_r values at a given α value increase with temperature in the range of α from 0.1 to 0.5; and (2) from $\alpha = 0.1$ to 0.4 this increase is interrupted in the range 270–280°C, i.e., there is a leap in the position of the points between these temperatures.

Consequently, contrary to theoretical expectations, the experimental results of Fig. 5 show a relatively complex dependence of t_r on temperature. Our next task is, therefore, to find an explanation for this dependence.

With a rise in temperature the value of t and $t_{0.7}$ for a certain α value decrease. Since their ratio (t_r) increases, however, this means that t decreases more slowly than $t_{0.7}$. We shall try to connect this delay in the decrease of t with a specific peculiarity of the isothermal method when applied to the decomposition of solids. We have in mind the presence of an inevitable,

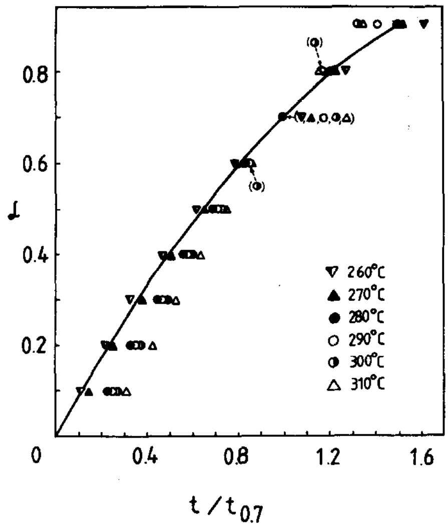

Fig. 5. Experimental α–t_r points for reaction (1) at $t_{0.7}$ and theoretical α–t_r curve according to eqn. (4).

initial non-isothermal period of the heating of the sample, and the container in which it is found, to the desired temperature. Reaction (1) in our case starts at ca. 250°C. If carried out at that temperature, there will be no such period, because no process occurs until the tempering of the sample is attained. At any higher temperature, however, it will exist, which indicates that part of the substance always decomposes non-isothermally at temperatures lower than the given one, and that this relative delay of the process gradually increases with temperature.

This concept can also be examined on a more general basis by making use of eqn. (3), from which it follows that

$$t_{0.7} = 0.4523/k_T \tag{5}$$

or, in a general form,

$$t_i = \mathrm{const}_i/k_T \tag{6}$$

where t_i is the time necessary to attain $\alpha = i$ (in our case $i = 0, 0.1, 0.2, \ldots 1$). The ratio of t_i to $t_{0.7}$ for an arbitrary temperature in the range under review in an ideal case when there is no initial non-isothermal period is

$$t_r = \frac{\mathrm{const}_i/k_T}{0.4523/k_T} = \mathrm{const}'_i \tag{7}$$

i.e., t_r does not depend on temperature. Under real conditions, however, an initial non-isothermal period exists during which the decomposition proceeds at different values of the rate constant, k_{T_1}, k_{T_2}, $\ldots$, until an isothermal regime with k_T ($k_{T_1} < k_{T_2} < \ldots < k_T$) has been established. In this case it is convenient to introduce an effective value for the rate constant k_{T_i} ($k_{T_i} < k_T$), which, for t_i, would realize $\alpha = i$. The value of k_{T_i} for different α at a certain temperature differs, because the ratio between the quantity of the non-isothermally and the isothermally decomposed substance differs (k_{T_i} tending toward k_T with an increase in α). In this case eqn. (7) therefore assumes the form

$$t_r = \frac{\mathrm{const}_i/k_{T_i}}{0.4523/k_T} = \mathrm{const}'_i \frac{k_T}{k_{T_i}} \tag{8}$$

from which it can be seen ($k_{T_i} \neq k_T$) that t_r is a function of the rate constant, i.e., of temperature, something which we found experimentally. It is only for $i = 0.7$ that t_r will not depend on temperature and all points will merge into one (Fig. 5). For $i > 0.7$, t_r again depends on temperature, but now inversely: with a rise in temperature, t_r decreases, which, likewise, is in agreement with our experiments.

At temperatures close to that of the beginning of decomposition (ca. 250°C) the dependence of t_r on T is less pronounced and eqn. (8) approaches eqn. (7). On this basis the theoretical α–t_r curve calculated from eqn. (4) should pass close to the points for these temperatures. The theoretical curve thus plotted (Fig. 5) does, indeed, correspond to the points for 260 and 270°C.

The examined dependence of t_r on T leads to two deductions of practical significance: (1) the even shift of the points for the experimental α–t_r curve at constant α with a rise in temperature reflects the specificity of the isothermal method under real conditions and therefore does not imply a violation of the isokinetic course of the respective process; (2) the tracing of the α–t_r curve on the experimental points of the examined variant (at constant α values) should not be done by averaging t_r, as the scattering of the points is not a result of errors. Its drawing calls for attention to lower temperatures and a possible comparison with the theoretical α–t_r curve on the basis of the equation of a preselected kinetic model of the process.

Since eqn. (7) is valid for an arbitrary temperature in the given range, if there should be changes in the mechanism of the process, such as only occur when the temperature changes regardless of their character (i.e., whether the rate law changes or not), this equation remains in force. Consequently, such changes in the reaction mechanism could not, in principle, be reflected on t_r, and thus on the corresponding α–t_r curves. Equation (7) calls, however, for a strictly isothermal process. Under real conditions, however, owing to the initial non-isothermal period, this condition is not observed, so that eqn. (7) is inapplicable in this case. We can therefore attempt to connect the leap in the disposition of the points between 270 and 280°C with the reaction's (1) non-isokinetic character (Fig. 4). It should be borne in mind that Fig. 4 is a result of our previous investigations [14] and that the indicated temperature (ca. 280°C) of change of the Arrhenius plot is only approximate. At such a disposition of the points of the second Arrhenius straight line, the latter can, with the same probability, be traced with a steeper incline, so as to intersect the first straight line between 270 and 280°C.

The effect of the non-isothermal period up to 270°C manifests itself in a manner which has already been considered. At about 280°C, after the non-isothermal period and the tempering of the sample at that temperature, the process suddenly continues with a rate constant of $k_{\sim 280}$, which is inferior to the value it would have if the Arrhenius plot had preserved its initial incline. This introduces a new relative delay into t_i, giving rise to the pause observed in t_r between 270 and 280°C. At higher temperatures the process is carried out at a rate constant value in agreement with the second incline of Fig. 4. Consequently, perhaps for the first time, the non-isothermal period plays a positive role, since it allows the non-isokinetic character of reaction (1) to manifest itself in its experimental α–t_r curve, which in the absence of such a period would not, according to theory, be observed on that curve. On the other hand, since the magnitude of the non-isothermal period also depends on certain experimental conditions, such as mass of sample and container and sign and value of the heat of the process, the observed effect should also be affected by these factors. In our case it is favoured by the

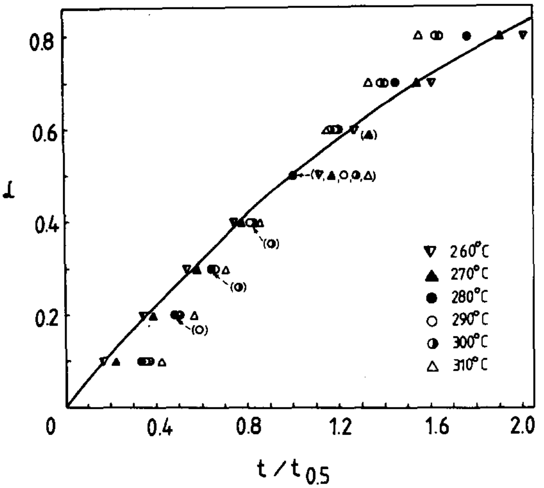

Fig. 6. Experimental $\alpha - t_r$ points for reaction (1) at $t_{0.5}$ and theoretical $\alpha - t_r$ curve according to the equation: $1-(1-\alpha)^{1/2} = 0.2929\ t_r$ [10].

relatively large mass of the sample (1 g) and the considerable endoheat given out by the process, chiefly representing a sum of the endoheats of the two elementary processes of reaction (1): dehydrogenation and partial reduction of Co^{3+} to Co^{2+} [24].

Since $k_{T_i} \rightarrow k_T$ with an increase in α at a certain temperature, eqn. (8) approaches eqn. (7). In practice this implies that the points in Fig. 5 move closer together with an increase in α, which, in turn, narrows the region for an analysis of the disposition of the points within the limits for $\alpha = 0.1$–0.4

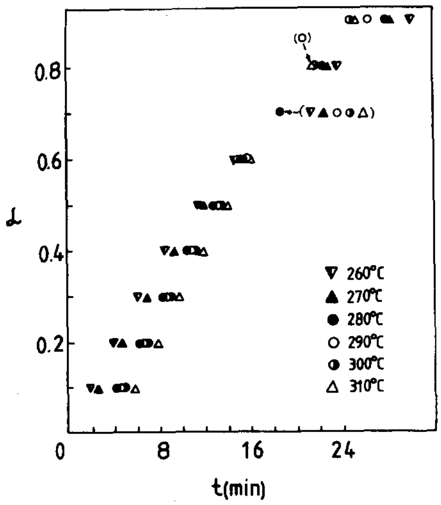

Fig. 7. Experimental points for reaction (1) using a standard curve at 280°C and a common point at $\alpha = 0.7$.

or even for $\alpha = 0.1$–0.3 in Fig. 6 ($t_{0.5}$). Our attempts to extend this region by means of $t_{0.8}$ and $t_{0.9}$ proved futile.

The points obtained for reaction (1) by means of the standard curve at 280°C and the common point at $\alpha = 0.7$ are shown in Fig. 7 for the sake of comparison. As can be seen, there is no difference in character between Figs. 5 and 7.

CONCLUSION

The ideas developed on reduced-time plots of the process investigated amount to what we consider to be a relatively well-grounded hypothesis. Considerable investigations of other processes are still necessary to shed light on the deductions made here, and possibly to confirm or reject them. Its significance resides mainly in that it directs attention to a more detailed examination of α–t_r curves with a view to linking them with the kinetic particularities of the processes investigated. On the other hand, these curves can be used more widely as regards the effect of other factors at constant temperature, for instance, sample irradiation [5]. They might also be applied to the remaining topochemical processes of the type $A_{(s)} + B_{(g)}$ [25] and $A_{(s)} + B_{(s)}$, at which it is possible to temper the reacting phases to the experimental temperature beforehand, so as to avoid the initial non-isothermal period.

We also believe that the reduced-time plots could also be used in homogeneous kinetics, thus acquiring the character of a general method for expressing isothermal kinetic data.

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