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EFFECT OF THE DISPERSITY OF SUBSTANCES ON THE MACROKINETICS OF THERMAL ANALYSIS UNDER NON-ISOTHERMAL CONDITIONS

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The effect of the dispersity of the sample on the topochemical mechanism and on the kinetic parameters of thermolysis ($A_s \rightarrow B_s + C_g$) under non-isothermal conditions is discussed. For correctness of the experiment, a ratio of maximum and minimum particle diameters ≤ 6 is a necessary condition. The topochemical mechanism of the process should be determined separately for the initial and final stages.

In all monographies discussing the kinetics of heterogeneous processes under isothermal conditions much attention is paid to the effect of the dispersity of the substance on the character of the rate-controlling stage of the process ([1–3] and others), and monodispersity is assumed in the deduction of many topochemical rate equations.

On the other hand, in the majority of experimental work studying the kinetics of thermolysis processes $A_s \rightarrow B_s + C_g$ under non-isothermal conditions, the necessity of monodisperse samples is disregarded. This peculiar feature is presumably connected with the historical development of experimental non-isothermal kinetics not based on the methods and concepts of the chemistry of solids, but on attempts of quantitative processing of thermal curves (DTA, TG) obtained in standard thermoanalytical experiments at linear heating rates. It may be observed that in some cases the preparation of the samples for thermal analysis by DTA includes grinding of the specimen to the "powder" state (<4.3 μm), while for clay minerals the fraction <1 μm is recommended [4].

However, in highly disperse materials, intergranular and intragranular diffusion exchange begins to play an important part. Under such conditions, the rate-controlling stage is diffusion of the evolved gases from the reaction zone to the surface of the particle, or from the internal part of the powder-like sample to its external surface [3].

In addition, as estimated by Delmon, the kinetic curves of homothetic shrinkage of the polydisperse sample up to conversions of 50% coincide with the kinetic curves of monodisperse samples only if the range ratio between the particle diameters does not exceed the value of 6 ($d_{max}/d_{min} \leq 6$). In the case of a wider particle spectrum ($d_{max}/d_{min} > 6$) the order of the reaction increases to $n = 1$ and $n > 1$ [1]. Possibly such a wide range of dispersity yields the explanation for the frequent appearance of formal orders or reactions $n = 1$ and $n > 1$ in various papers (cf. e.g. [5–15]).

We studied the macrokinetics of the dehydration of the EDTA chelate MgMnL · 9 H_2O for samples with different particle sizes. The experiments were carried out in a continuous-flow reactor using a conductometric detector [16]; $m = 10.0$ mg, helium flow rate through the sample 60 cm^3/min, rate of temperature rise 3°/min. The analysis of the topochemical mechanism and the calculation of the kinetic parameters was performed by the evolved gas curves using the integral method with the computer program TA IB [17–20]; the best kinetic equation was selected on the basis of the linearity of the relationship $\lg g(\alpha)$ *vs.* $1/T$, for the conversion ranges $0.08 < \alpha < 0.030$; $0.30 < \alpha < 0.80$; $0.80 < \alpha < 0.95$. The successive widening of the ranges was chosen in view of keeping the error in the calculated value of the activation energy E within the limits of ±5%.

As may be seen from Table 1, scattering of the activation energy values for the fractions 80 . . . 400 μm does not exceed 2.5% (in all cases up to conversion of 50% the rate-controlling stage is the reaction on the phase boundary, $d\alpha/dt = k(1-\alpha)^{2/3}$).

When passing to fractions <80 μm, the process is apparently more and more retarded by diffusion. At $d < 50$ μm intergranular diffusion (best described by the Komats–Uemur equation) becomes the rate-controlling stage. Towards the end of the process ($\alpha > 50\%$) rate is controlled in all investigated cases by the diffusion of water vapour through the layer of the dehydrated product on the surface of the particles (best described by the Brounshteyn equation).

The data in Table 1 (and also our earlier published data: thermolysis of clathrates of thiourea, urea, hydroquinone, dehydration of EDTA chelates [20–22]) demonstrate that if the process $A_s \rightarrow B_s + C_g$ can be described at all by the equation of the reaction on the phase boundary ($n = 1/2$, $n = 2/3$), then only up to conversions of $\alpha = 50 \ldots 60\%$; at $\alpha > 60\%$ diffusion of the gas C through the layer of the product B_s on the surface of the particles becomes the rate-controlling factor. Hence, similarly as in isothermal kinetics, a fraction should be chosen where the ratio of extreme particle dimensions does not exceed 6 ($d_{max}/d_{min} \leq 6$). This will prevent distortion of the equation of the homothetic shrinkage of the particles up to conversions of 50% and yield reproducible values of E within error limits of 5%. No essential advantage ensues from the choice of a narrower fraction: the rate-controlling factor at conversions $\alpha > 50 \ldots 60\%$ will invariably remain diffusion through the product layer.

Kinetic parameters calculated from experimentally determined formal orders of reaction $n = 1$ (or $n > 1$) for polydisperse samples should be considered with caution, since the equation $d\alpha/dt = k(1 - \alpha)$ may express not only accidental nucleus formation, but may be a distorted form of the rate equation of the homothetic shrinkage of the particles due to rapid knock-out of the fine fraction [1].

The risk of error in evaluating the topochemical mechanism increases, if the order of reaction n is determined from the total kinetic curve. In fact, if the value of the formal order of reaction is calculated from the total dehydration curve established in our present experiments (Table 1), $n = 0.85 \pm 0.5$ for all narrow

Table 1

Kinetics of dehydration of the EDTA chelate (various fractions)
$MgMnL \cdot 9H\ O \rightarrow MgMnL + 9H_2O$

Fraction, μm	Topochemical mechanism	Conversion range α, %	E_a, kcal/mol	lg A	n (from the total curve)
315—400	Shrinking sphere	0.5—48.9	32.8	16.6	0.80
200—315	Shrinking sphere	3.5—44.1	32.0	16.1	0.80
160—200	Shrinking sphere	0.5—58.4	32.1	17.0	0.80
125—160	Shrinking cylinder	0.5—47.8	32.9	16.8	0.80
100—125	Shrinking sphere	0.5—48.1	32.9	16.6	0.80
90—100	Shrinking sphere	0.5—51.5	33.2	16.9	0.90
80—90	Shrinking sphere	0.5—52.5	31.7	17.0	0.80
71—80	Shrinking sphere	0.5—57.6	29.6	14.8	0.80
63—71	Shrinking sphere	0.5—80.4	28.1	13.7	0.90
50—63	Shrinking sphere	0.5—79.4	27.1	13.3	0.80
10—50	Three-dimensional diffusion	3.0—49.2	44.7	23.9	0.90
80—400	Shrinking sphere	0.5—52.0	32.1	16.5	0.80
Ground sample not separated into fractions (10—400)	Shrinking sphere	0.5—82.0	24.0	11.2	1.05

fractions. This distortion of the kinetic equation ($n > 2/3$) is caused by including the diffusion part of the process in the calculation of n. For a sample that is ground, but not separated into fractions, the formal order of reaction (owing to rapid knock-out of the fine fraction) rises to a value of $n = 1.05$, in agreement with the theoretical consideration of Delmon [1]: the calculation based on the equation of shrinking spheres results in a sharp decrease of the value of E_a when the process takes place in the range combined with diffusion.

References

1. B. Delmon, Introduction à la cinétique hétérogène, Paris 1969.
2. P. Barret, Cinétique hétérogène, Paris, 1973.
3. E. A. Prodan, M. M. Pavlyuchenko and S. A. Prodan, Zakonomernosti topokhimicheskikh reaktsy (Laws of topochemical reactions), Minsk, 1976.
4. V. P. Ivanova, B. K. Kasatov, T. H. Krasavina and E. D. Rozinova, Termichesky analiz mineralov i gornykh porod (Thermal analysis of minerals and rocks)., Izd. Nedra, Leningrad, 1974.
5. S. R. Dharwankar and M. D. Karhanavala, J. Indian Chem. Soc., 45 (1968) 490.
6. A. V. Shkarin, N. D. Topor and G. M. Zhabrova, Zh. fiz. khimii, 42 (1968) 2832.
7. J. Györe and M. Ecet, J. Thermal Anal., 2 (1970) 397.
8. R. Tsuchiya, A. Uehara and E. Kyuno, Bull. Chem. Soc. Japan, 44 (1971) 701.
9. P. M. Madhusudan et al., Thermochim. Acta, 9 (1974) 149.
10. N. R. Chandhum and S. Mitra, Bull. Chem. Soc. Japan, 48 (1975) 2837.

11. J. Zsakó, Cs. Várhelyi and G. Liptay, Thermal Analysis Proc., Akadémiai Kiadó, Heyden and Son, Budapest, 1974, 1, p. 825.
12. N. Raychaudhuri, G. K. Pathak and S. Mitra, Thermal Analysis Proc., Akadémiai Kiadó, Heyden and Son, Budapest, 1974, 1, p. 615.
13. N. Niklewicz, J. Warczak and N. Hajduk, Thermal Analysis Proc., Akadémiai Kiadó, Heyden and Son, Budapest, 1974, 1, p. 487.
14. I. M. Criado and I. Morales, Thermochim. Acta, 16 (1976) 382.
15. R. S. Kalyoncu, M. E. Tadros et al., J. Thermal Anal., 9 (1976) 233.
16. V. A. Logvinenko and L. I. Myachina, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. 9 (1974) 85.
17. F. Škvara, J. Šestak and V. Šestaková, Thermal Analysis Proc., Akadémiai Kiadó, Heyden and Son, Budapest, 1974, 1, p. 105.
18. V. Šatava and F. Škvara, J. Am. Ceram. Soc., 52 (1969) 11.
19. V. Šatava, Thermochim. Acta, 2 (1971) 423.
20. A. V. Nikolaev, V. A. Logvinenko, Ya. Shestak and F. Shkvara, Dokl. Akad. Nauk SSSR, 231 (1976) 146.
21. V. A. Logvinenko, O. V. Gegola, G. N. Chekhova and Yu. A. Dyadin, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., 9 (1977) 95.
22. V. A. Logvinenko, O. V. Gegola, G. N. Chekhova and Yu. A. Dyadin, Soveschanie po kinetike i mekhanizmu khimicheskikh reaktsy v tverdom tele (Conference on the kinetics and mechanism of chemical reactions in solids), Novosibirsk, 1977. Thesises of the lectures, Part 1, p. 150.

Résumé — L'effet de la dispersion de l'échantillon sur le mécanisme topochimique et sur les paramètres cinétiques de la thermolyse ($A_s \rightarrow B_s + C_g$) en conditions non-isothermes est discuté. La conditions nécessaire pour qu'une expérience soit correcte est que le rapport entre les valeurs maximale et minimale des diamètres des particules soit $\leqslant 6$. Le mécanisme topochimique du processus devrait être déterminé séparément pour les étapes initiale et finale.

Zusammenfassung — Die Wirkung der Dispersion der Probe auf den topochemischen Mechanismus und die kinetischen Parameter der Thermolyse ($A_s \rightarrow B_s + C_g$) unter nichtisothermen Bedingungen wird diskutiert. Die Genauigkeit des Experiments setzt ein Verhältnis der maximalen und minimalen Teilchendurchmesser von ≤ 6 voraus. Der topochemische Mechanismus sollte für die Anfangs- und Endphase des Vorganges einzeln bestimmt werden.

Резюме — Рассмотрено влияние дисперсности образца на топохимический механизм и кинетические параметры термолиза ($A_{\text{тв}} \rightarrow B_{\text{тв}} + C_{\text{газ}}$) в неизотермических условиях. Для корректного эксперимента допустимым является отношение размеров максимального и минимального зерна $d_{\text{макс.}}/d_{\text{мин}} \leqslant 6$; топохимический механизм процесса должен определяться отдельно для начальной и конечной стадий.