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Heat- and mass-transfer approach to decomposition kinetics [α,β]

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Abstract

Despite justifiable doubts concerning applicability of the Arrhenius equation to reversible thermal decomposition of solids, a viable alternative is lacking. This paper is intended to contribute to the general discussion in this area and to propose a new approach, based on a combination of diffusion and heat transfer, with the Clausius–Clapeyron equation. Reversible decompositions of hydrates of copper and magnesium sulfates have been studied in a broad range of the inhibition of the reactions by their volatile products: from microgram-size samples in vacuum, to multi-gram samples in self-generating atmosphere; and with varying rate of heat transfer. A simple interpretation of the shape of TG curves based upon transport processes, antithetical to the kinetic one, is proposed. Also a new definition for decomposition temperature is proposed.

INTRODUCTION

It has been documented in the literature [1–12] that kinetic parameters A and E, calculated for gas-evolving reversible thermal decomposition of solids in most cases have little or no physical meaning; and that kinetic interpretation of thermoanalytical data (especially for non-isothermal experiments) cannot be done in a rigorous manner. The formally simple process

$$A_{solid} \rightleftharpoons B_{solid} + C_{gas}$$

is actually a very complex one, as it consists of more than a dozen elementary processes in each direction.

Most of the methods result from using the Arrhenius equation, combined with various kinetic equations. This seems natural, because reaction rate depends on temperature, and on how the rate changes with progression of the process α. The latter function $f(\alpha)$ or its integral form $g(\alpha)$ is a major obstacle here, as it is usually unknown and difficult to determine.

[α] Presented at the 19th Annual NATAS Conference, Boston, MA, 23–26 September 1990.

[β] Dedicated to Professor Paul D. Garn.

The Ozawa [20], and Flynn and Wall [14] methods, or iso-conversional method, circumvent that problem successfully, as they do not require knowledge of the form of $f(\alpha)$. Nevertheless, for many substances the discrepancies and inconsistencies are large, and the calculated values are sometimes obviously meaningless (e.g. negative activation energy). Authors admit that neither the Arrhenius equation (derived for collisions of molecules in homogeneous systems), nor the implied concept of an active complex, make sound bases for non-homogeneous reactions. Still, no better basis is in sight.

The term "kinetics" is sometimes confusing, because some thermal analysts mean micro-kinetics (molecular or intracrystalline level; this is where activation energy applies), while others mean macro-kinetics (the whole-sample level). Obviously, in thermal analysis only the latter is recorded. There is no question that micro-kinetic processes (including activated ones) do take place in the discussed processes, but only the slowest one is manifesting itself as the actual (measured) reaction rate.

To minimize the adverse influence of transport processes, the established kinetic practice [15] requires studying samples as small as possible. Experience shows, however, that even very small samples are sometimes far from small enough not to be diffusion controlled [2–5,8]. Another disadvantage of small samples is that they provide poor correlation with large-scale processes. It is generally agreed that activation energy calculated for reversible thermal decomposition of solids is a procedural value of no real physical meaning. It is merely a number characterizing the individual thermoanalytical case (not the generic process). These limitations and problems have been recognized by the Kinetics Committee of I.C.T.A. [13].

Published data and discussions indicate that there are cases where the Arrhenius equation applies well, and other cases where it does not [6,7]. Reliable kinetic results are often produced by thermal analysis, e.g. of polymers, but those processes evidently do not fall into the class discussed (they are irreversible). Maciejewski [2–5] gives comprehensive reviews and critical discussion of the issues of transport processes in thermal analysis; he strongly stresses the influence of the partial pressure of the volatile product, and gives unequivocal evidence on how dramatically kinetic parameters can be affected by the presence of the gaseous product, rendering those parameters "meaningless and of little use".

The partial pressure of the gaseous product is often discussed, meaning the partial pressure imposed on the sample from the outside. The partial pressure generated by the material, as well as its diffusion is discussed usually on the single-grain level (i.e. through the layer of a product on the surface of the decomposing substrate). The issue of the concentration of the gaseous reaction product in the vicinity of grains, and in the whole sample is discussed less frequently. The works of Garn [7] and Šesták [12] represent opposing views on gas-evolving thermal decomposition of solids, and they exemplify the dramatic lack of consensus in this matter.

The fact that the kinetic apparatus based on the Arrhenius equation is being used in the area of gas-evolving reversible thermal decomposition is generally explained by the need to use the best available methods, even if they are not perfect. It can be argued that if we agree that the Arrhenius equation is inadequate for diffusion-controlled reversible thermal decomposition, the natural consequence will be to switch to the adequate language of the equations pertaining to diffusion, and of the Clausius–Clapeyron equation.

This paper is focussed on experimental determination of whether, and under what conditions, micro- or macro-kinetic factors prevail in two well-known decomposition cases, that of copper sulphate pentahydrate, and of magnesium sulphate heptahydrate. That is whether, and when, it is legitimate to use any Arrhenius-equation-based model.

EXPERIMENTAL

A Cahn thermogravimetric system TG-131 was used. This instrument was selected because of its broad range of sample size (1 mg to 100 g) combined with the 1 μg resolution, and its environment flexibility. A set of sample holders was used, featuring a broad range of hinderance of escape of volatile products and the capability to isolate the influence of heat transfer. The set consisted of five sample holders, shown in Fig. 1. Four kinds of environment were used: nitrogen at ambient pressure, flowing 50 ml min^{-1}; nitrogen saturated with water vapor, total flow 50 ml min^{-1}; vacuum (0.001 mbar); self-generating atmosphere (sample holder no. 5).

Comparative experiments, with heat-flow capacity being the only variation, were done to compare the influence of heat transfer. The combination of diffusion-affecting factors, with those affecting the heat transfer, allowed the assessment of those influences. Initial portions of TG curves of copper sulfate pentahydrate and magnesium sulfate heptahydrate were recorded and plotted as weight percent versus temperature, as families of curves. The curves are shown and explained in Figs. 2–5.

DISCUSSION

The initial stages of thermal decomposition of hydrates of copper and magnesium sulfates were studied over a broad range of magnitude of factors, potentially inhibiting the reaction by their volatile products. The limitation to the initial stages results from the unavoidable loss of compactness of the material after some initial mass loss, rendering the degree of diffusion hinderance uncontrollable.

In the case of the hydrates studied, the kinetics of these decompositions seem to be controlled by the rate of escape of the gaseous product C. This can be seen in Figs. 2 and 3, where even at ambient temperature the

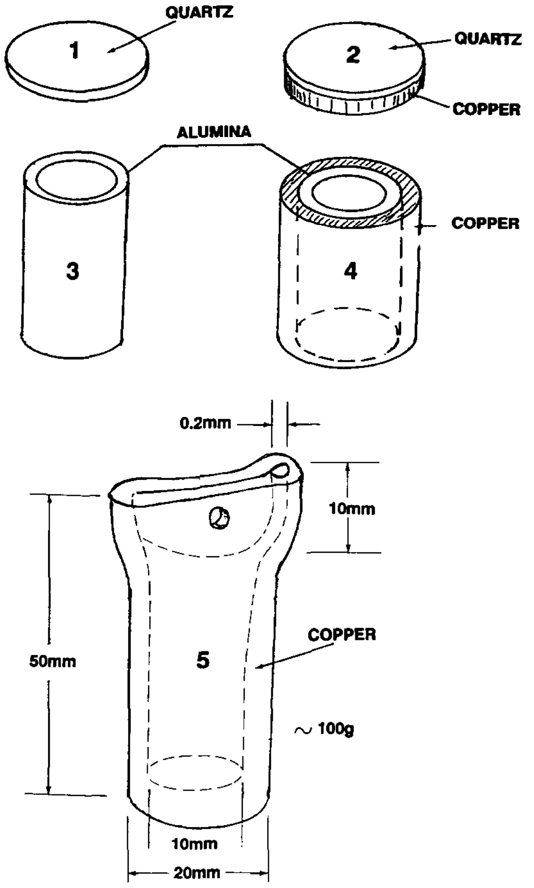

Fig. 1. Sample holders used to determine the influence of diffusion and of heat transfer on reversible thermal decomposition of hydrates of copper and magnesium sulfates. 1, horizontal flat quartz disk (0.5 mm × 25 mm diameter); 2, horizontal flat quartz disk (0.5 mm × 25 mm diameter), placed on a copper disk (10 mm × 25 mm diameter) – the copper is used as a heat-flow buffer; 3, narrow alumina cylinder (20 mm high, 10 mm internal diameter); 4, narrow alumina cylinder (20 mm high, 10 mm internal diameter), placed in a cylindrical copper envelope (5 mm walls); 5, cylindrical copper container (20 mm outer diameter, 10 mm internal diameter, 50 mm high, mass approx. 100 g), with outlet restricted to a channel of 0.2 mm internal diameter, 10 mm long.

decomposition is fast, provided the volatile product is being removed fast enough. Otherwise, the decomposition is almost stopped, and the substrate (erroneously) seems much more stable. It would look unreasonable to attribute those differences to any micro-kinetic interpretation. The same can be said as the result of comparing the curves of Figs. 4 and 5: A versus B, D versus B, E versus F, and G versus H. A strong dependence of the thermal decomposition on diffusion seems evident. Let us explain that whenever diffusion is discussed in this paper, the escape rate of the volatile product, both from the immediate vicinity of grains and from the sample holder, is

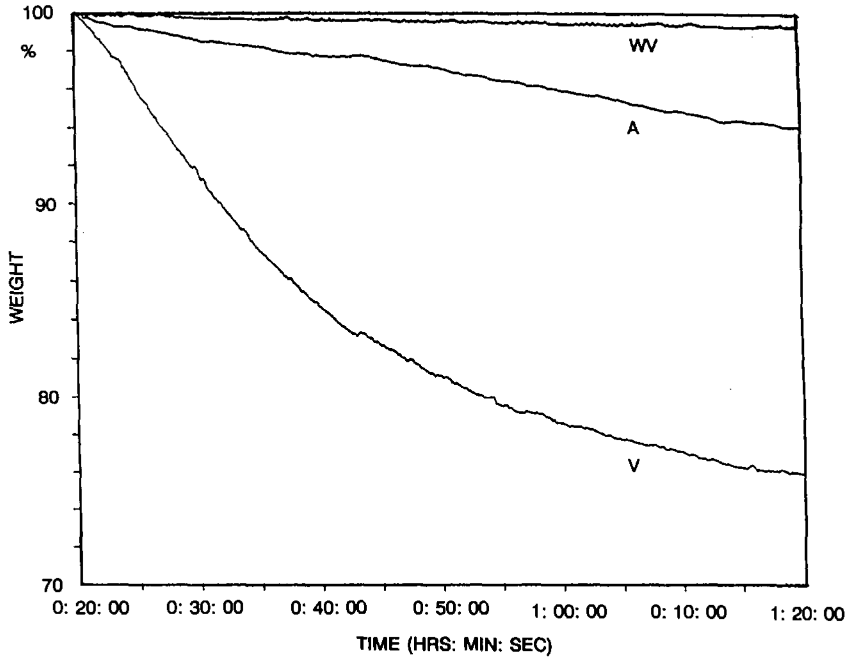

Fig. 2. Isotherming mass recording of 4 mg copper sulfate pentahydrate, kept at room temperature in container 1: A, in nitrogen at ambient pressure; WV, in nitrogen at ambient pressure saturated with water vapor; V, in vacuum.

meant, as opposed to diffusion of that gas inside the grains. Obviously, the controlling factor will be the concentration (partial pressure) of that gas, but diffusion acts here as a complementary equivalent for that concentration.

A gas-evolving, reversible thermal decomposition resembles in many respects the process of removing of vapor from the surface of its liquid. Both thermal decomposition (the kind discussed) and evaporating/boiling liquids behave in the same way; only the corresponding values of the equilibrium vapor pressure are always higher for liquids, than for the same kinds of vapor, when released by breaking of chemical bonds. One method for determining saturation vapor pressure of a liquid utilizes TG, DTA or DSC instruments. A sample of a liquid is loaded into a sealed aluminum capsule and a pinhole is made in the lid. In such a sample holder the saturation is attained immediately, and the slow escape through the pinhole is quickly compensated by more evaporation. When heated gradually, the liquid increases its evaporation rate only insignificantly, controlled only by the changing dependance of diffusion (in the pinhole area) on temperature. The internal pressure in the vessel remains almost constant and is only slightly higher than ambient. What is changing is the partial pressure of the vapors, rising on the expense of the entrapped air, that air diffusing out, together with the vapors. When the value of the partial vapor pressure has reached

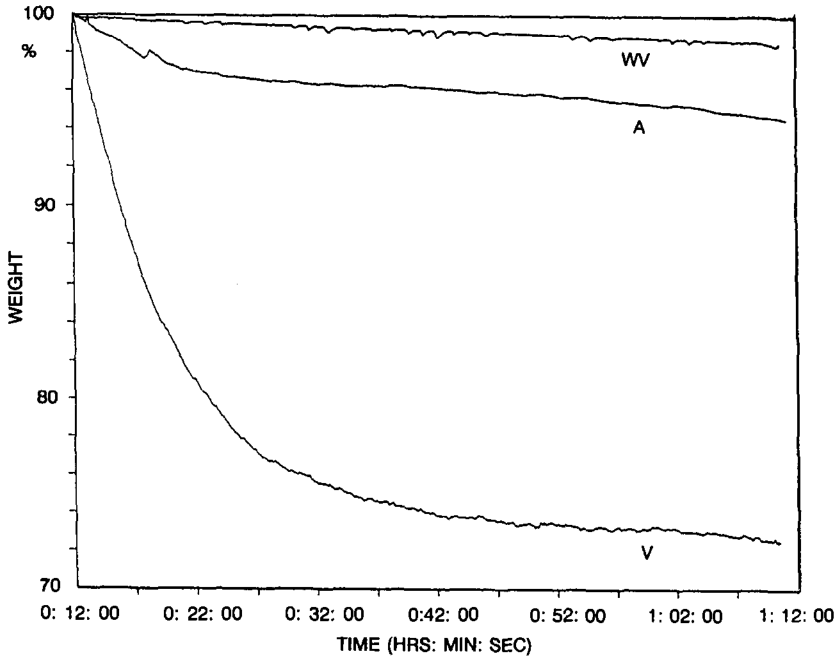

Fig. 3. Isotherming mass recording of 4 mg magnesium sulfate heptahydrate, kept at room temperature in container 1: A, in nitrogen at ambient pressure; WV, in nitrogen at ambient pressure saturated with water vapor; V, in vacuum.

the ambient, it cannot rise any further, and the evaporation turns into boiling. The corresponding thermoanalytical peak (there can be a plateau on the top of that peak) produces a reasonably accurate value of the boiling point. If it is studied at several values of the pressure, a logarithmic dependance of the saturation vapor pressure on temperature is easily and quickly obtained.

Such a procedure of obtaining volatility information about liquids can be extended into the field of gas-evolving thermal decomposition of solids. What we record in regular TG curves (other than those obtained in a self-generating atmosphere) is an equivalent for the evaporation of a liquid below its boiling point.

In any reversible, gas-evolving, reaction the term "temperature of decomposition" is very ill-defined and highly confusing, but it does not need to be. For a non-gas-evolving reaction $A_{solid} \rightleftharpoons B_{solid}$ it would be the temperature borderline, below which the substance A is stable, and above which the B substance is stable. However, for the reaction discussed $A_{solid} \rightleftharpoons B_{solid} + C_{gas}$, following the Clausius–Clapeyron law), the equilibrium temperature depends on the partial pressure of the gas C. The equilibrium temperature and the equilibrium pressure are mutually dependent upon each other. Therefore at any temperature higher than absolute zero, there is no distinct tempera-

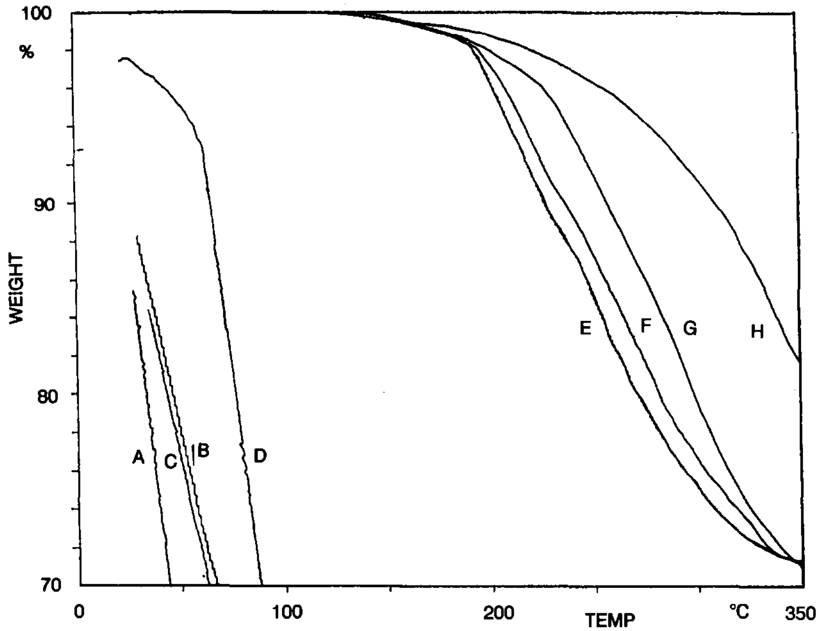

Fig. 4. TG curves of copper sulfate pentahydrate: A, 350 μg copper sulfate in container 1 in vacuum; B, 3 mg copper sulfate in container 1 in nitrogen; C, 3 mg copper sulfate in container 2 in nitrogen; D, 3 mg copper sulfate in container 1 in nitrogen saturated with water vapor; E, 1.4 g copper sulfate in container 3 in nitrogen; F, 1.4 g copper sulfate in container 3 in nitrogen saturated with water vapor; G, 1.4 g copper sulfate in container 4 in nitrogen; H, 2.6 g copper sulfate in container 5 (self-generating atmosphere). Curves A–D obtained at heating rates of 2°C $\min^{-1}$ and curves E–H at 10°C $\min^{-1}$.

ture which can be called a decomposition temperature. The only value standing out from the others would be the equilibrium temperature at 101.3 kPa, that is at ambient pressure. The "temperature of decomposition" (represented as the "beginning of thermal decomposition") is strictly procedural, and should not be interpreted as the decomposition temperature, in the same way that the beginning of a thermoanalytically-recorded evaporation of a liquid below its boiling point would be a merely procedural value, lacking any absolute physical meaning. Thermoanalytical literature abounds in examples for this fact. Figures 2 and 3 demonstrate the same: the hydrates of sulfates of copper and magnesium, commonly believed to be stable at room temperature, decomposed quickly if the water vapor was removed quickly enough (both from the reaction front and from the sample holder).

In the same way as a liquid evaporates below its boiling point, the increasing vapor concentration between the grains of the sample is consumed by diffusion-type escape from between the grains of the material, through the neck of the sample holder, and throughout the ambient gas. It is a negative feedback situation: if the concentration of vapors at each point

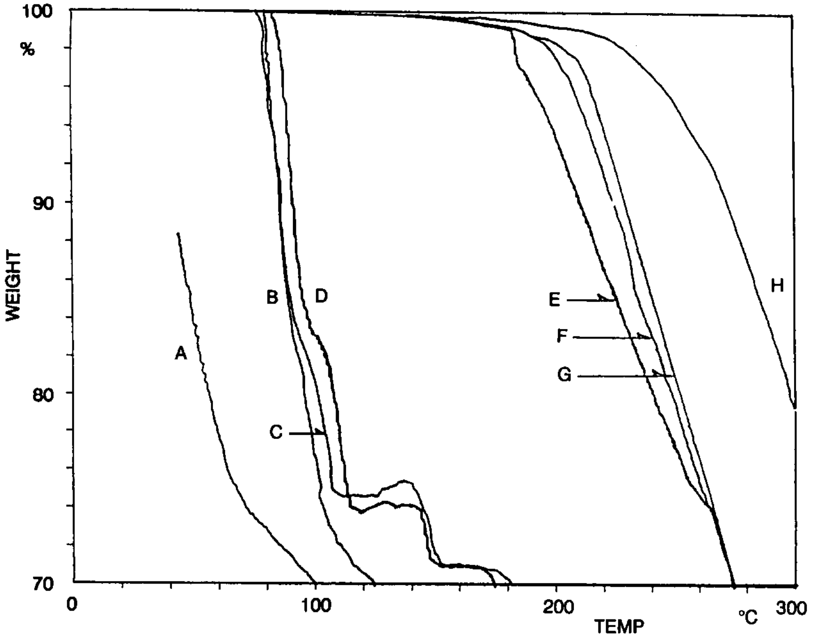

Fig. 5. TG curves of magnesium sulfate heptahydrate: A, 350 μg magnesium sulfate in container 1 in vacuum; B, 3 mg magnesium sulfate in container 1 in nitrogen; C, 3 mg magnesium sulfate in container 2 in nitrogen; D, 3 mg magnesium sulfate in container 1 in nitrogen saturated with water vapor; E, 1.7 g magnesium sulfate in container 3 in nitrogen; F, 1.7 g magnesium sulfate in container 3 in nitrogen saturated with water vapor; G, 1.7 g magnesium sulfate in container 4 in nitrogen; H, 3.2 g magnesium sulfate in container 5 (self-generating atmosphere). Curves A–D obtained at heating rates of 2° C min^{-1} and curves E–H at 10° C min^{-1}.

restricts decomposition, then less vapor is generated; as the vapors get dispersed further decomposition is allowed. As the temperature rises (we are discussing linear heating), so does the heat flow to the sample, the reaction rate and the escape rate, making the slope of the TG curve steeper. This continues until too little of the undecomposed material is available to support the concentration of vapors, but enough remains to be a solely restrictive step. At this point the local decomposition rate increases further for a very short period of time, then it drops to zero because of the completion of the reaction. That sudden, short-lived local increase in the reaction rate may be masked and consumed by the generally finished reaction, because that “burst” takes place only locally, in a very small, residual area.

If the escape is strongly hindered, the conditions for “self-generated atmosphere” are created. Like evaporation of a liquid in a pinholed capsule, in self-generating atmosphere conditions, saturation is attained immediately, and slow loss of the gas, escaping between the grains and through the narrow outlet is quickly compensated by more decomposition. When heated gradually, the decomposition increases its rate only insignificantly, being controlled only by the changing dependence of diffusion on temperature. The total internal pressure in the sample holder remains almost constant and is only slightly higher than the ambient. What changes, is the partial pressure of the vapors, which rises at the expense of entrapped air, the excess of which is diffusing out, together with some vapors. When the value of the partial vapor pressure has reached the ambient (not 1 atm, but any pressure existing inside the instrument), the pressure cannot rise any further, and the diffusion turns into a pressure-forced flow (viscous flow). The corresponding thermoanalytical peak (there can be a plateau on the top of that peak) provides data on the dependance of the equilibrium temperature on the equilibrium pressure. This dependance is the Clausius–Clapeyron equation in its reversed form; for the case discussed, pressure is the independent variable and temperature is the dependent one. A series of tests in self-generating atmosphere, at several values of ambient pressure, will produce the Clapeyron plot for this decomposition process.

If the conditions of pressure-forced flow have been achieved, from this point on, escape no longer depends on diffusion, but on heat transfer. Under isothermal conditions the pressure is almost constant, and the limiting step is now the supply of heat. This is what makes the mass-loss rate linear, or the DTG peaks cut-off by a plateau. This is an extreme case; the same phenomenon, but less radically pronounced is when both diffusion and heat transfer share (varying the magnitude of that share along the TG curve) the control, and the partial pressure of the volatile product almost reaches the ambient pressure. This is what causes TG curves to be sigmoidal (s-shaped). Such cases (both s-shaped and straight-sloped TG curves) have been discussed previously [8], and they are well-known in general kinetics (see, for example, ref. 16). By the way, general-kinetic researchers (unlike thermal analysts) take it for granted that equations of chemical kinetics must not be applied to diffusion-controlled processes.

Such “cut-off bell” cases are important both for the theory of thermal analysis, and for its industrial-scale projections and predictions. Many large-scale processes are likely to be close to conditions of self-generating atmosphere. Even more important, in view of the enormous extent of confusion in the area of thermoanalytical kinetics, which is plagued by highly unreliable results, the Clapeyron-plot data seem to be the only solid kind of information. A Clausius–Clapeyron plot can characterize gas-evolving, reversible thermal decomposition processes in an objective, reliable and repeatable way.

In non-isothermal experiments “cut-off bells” should be less common or less pronounced, because the increasing temperature imposes a continuing increase in flux of heat, the latter being the limiting step. However, practical results (including those presented in this paper (curves G of Figs. 4 and 5)) show that even for linear heating, such curves are not uncommon. The curves H of Figs. 4 and 5, obtained for sample holder no. 5, are curved much more than the curves G, indicating a significant overpressure build up, due to the capillary outlet.

If it were not for the extremely strong sample holder, it would probably burst. Similar cases are sometimes encountered with tightly packed or melting TG samples, pushed out like pistons from their cylindrical holders.

The existence of true self-generating conditions is a prerequisite for generation of Clausius–Clapeyron data. Isothermal mass recording seems to be the method of choice for obtaining such data, but linear heating can also produce reliable information, in a manner faster than isothermal mass recording. A really straight section of a TG curve, or a "cut-off-bell" DTG/DTA/DSC peak indicates a strong probability for the existence of self-generating atmosphere, and consequently of heat transfer being the controlling macro-kinetic mechanism. An even better criterion would be temperature ramping in a fast/slow/fast/slow pattern, and examination of whether the short periods of the heating-rate decrease result in a decrease in the decomposition rate. A positive answer would confirm the heat-flow as the controlling macro-mechanism, and also confirm the existence of conditions of self-generating atmosphere.

The model given here conflicts with those found in thermoanalytical literature [2,3,17–19]. The present consensus on the concept of "decomposition temperature" does not seem to be consistent. The term "decomposition temperature" is usually defined as the lowest temperature at which the rate of the decomposition is measurable; and marked as T_1. A "temperature of thermodynamic stability" (T_{th}) is defined as the temperature at which the partial pressure of the gaseous product equals the ambient pressure. It is said to be obvious that T_1 must be higher than T_{th}, for the decomposition to proceed. In view of the model given above in this paper, it is just the opposite. The opinion quoted above would be correct for the product C being the only gaseous component of the environment, but then the temperature of decomposition would not exist, as at any temperature other than absolute zero, the release of the gas (by definition) would remain in equilibrium with the same gas surrounding the substance, that is with the ambient pressure. If the gaseous product C is not the only component of the environment, but is mixed with an inert gas (e.g. air), and diffusion is allowed, the decomposition proceeds at any partial pressure of that product, ranging from zero to the ambient pressure. When the partial pressure of the gaseous product reaches the ambient, it is not decomposition that starts, but the "forced flow", discussed above. Therefore T_1 cannot be higher than T_{th}. Moreover, the large sets of "standard" TG curves, intended to be relied on as the basis for thermal processing, and meticulously generated and collected by Duval [18] and Liptay [19], turn out to be unreliable. The author of this paper once almost killed himself and several other people, when he trusted his thermoanalytical data on thermal stability. According to the TG curves of a thiocyanate complex, the thiocyanate component of that complex seemed perfectly stable below at least 250 ° C. When a kilogram-scale flow-through reactor, based on that data was built and used, the compound decomposed quickly at about 150 ° C, evolving cyanogen gas $(CN)_2$. That misleading apparent thermal stability turned out to be merely a hindered decomposition, unleashed by the flowing inert gas. In view of the decomposition model presented in this paper, such behavior is not an exception, but a rule.

One may argue that calcium carbonate indisputably does have some decomposition temperature, because it will not decompose even in vacuum below, say, 600 ° C. The explanation for that fact is that there is a temperature below which the synthesis of calcium carbonate is irreversible. Consequently, this case does not contradict the proposed model. However, this clarifies the concept of "decomposition temperature". In this way, everything said above about the non-existence of decomposition temperature above absolute zero remains valid provided the reaction remains reversible.

Let us propose a new definition for decomposition temperature. "In gas-evolving processes of thermal decomposition of solids, the term decomposition temperature applies only to irreversible decomposition. For reversible processes, the temperature of decomposition is the temperature below which the synthesis is irreversible." Thus, within the temperature range of reversibility, decomposition temperature does not exist.

The existence of a reaction front challenges the legitimacy of attributing micro-kinetic interpretation to thermoanalytical data obtained for an entire sample. This was pointed out by Garn [10] and other authors as early as 1965. Let us repeat this again: experience shows that milligram-size samples are not much closer to micro-kinetics than gram-size ones, the reaction

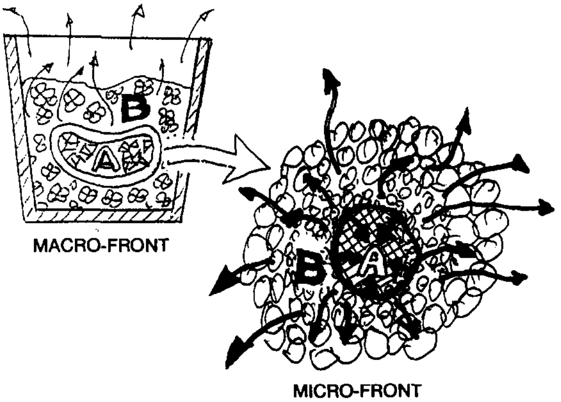

Fig. 6. Concurrent existence of a macro-front and a micro-front (inside the grains in the macro-front zone) in thermal decomposition of solids.

remains topochemical even for the smallest samples, and reaction fronts do exist. Let us add another clarification, that if there is a reaction front, then it really means at least two concurrent kinds of reaction front (both inwardly contracting around the unreacted domain of the substrate A): a "macro-front" around the A-substrate core of the entire sample, and a "micro-front" around the A-substrate core of each individual grain within the "macro-front". This concept of distinction between the macro-front and the micro-front is explained in Fig. 6.

With reaction front, the average values recorded in thermal analysis are meaningless for the actual (local) speed of the reaction. The best chance of knowing the value of local partial pressure of the gaseous decomposition product, is for self-generating atmosphere, as in this case the evolved gas is the only gaseous component in the vessel. The value of this pressure approximately equals the ambient; therefore it is known. (If it were lower, the reaction would progress and raise it; if it were higher, the excess of the pressure would be released to the outside.)

The dependance on heat transfer appears to exist only for decomposition under conditions closer to self-generating atmosphere (curves E versus G and B versus C of Figs. 4 and 5).

The case of just two hydrates should not be generalized. However, examples of exactly the same type of behavior are abundant in the literature, just their interpretation seems confusing.

Concern has been expressed [7] that because many materials (plastics above all) conform to kinetic models, those kinetic models are extrapolated to other classes of materials without proof and these may or may not conform.

Transport processes do belong to macro-kinetics; that is true. What seems disputable, is describing transport-controlled processes by the Arrhenius equation, which is valid only for chemical reactions. The existence of the Arrhenius equation does not prove its applicability to a given case; otherwise we would take the assumption for the proof.

The main postulate of this paper is encompassed in the following rules, which are proposed for thermal analysis of gas-evolving, reversible thermal decomposition of solids.

(1) In each case there is a requirement to determine whether the process under investigation is controlled by micro-, or by macro-kinetics, prior to applying Arrhenius-based kinetics, and to abandon the automatic assumption for the last.

(2) It should be recognized that unless the local (grain level) partial pressure of the gaseous product is known, the term "temperature of decomposition" has no physical significance. Similarly, because decomposition happens at any temperature, "thermal stability" is only a relative, poorly reproducible term, and predictions of stability are impossible. Such predictions may even lead to dangerous mistakes.

(3) For practical purposes, only two temperature points of TG curves can be considered to be characteristic for decomposition. (a) The transition from irreversibility to reversibility. This is recorded as the first detectable downward deviation from the initially horizontal baseline, for curves obtained with no diffusion hindrance (sample not larger than 1 mg, under vacuum). If such a point cannot be obtained because under vacuum that substance decomposes even at room temperature (no horizontal baseline), then that point does not exist in the studied temperature range. (b) The temperature at which the equilibrium pressure of evolving gases equals ambient pressure. This is recorded as the first detectable downward deviation from the initially horizontal baseline, for curves obtained under "self-generating atmosphere" (full diffusion hindrance, but diffusion is no longer the slowest process); the reaction is controlled by flow restriction and by flow of heat. This value is likely to be of industrial importance.

CONCLUSIONS

This paper suggests an alternative solution to the discrepancies discussed, and it will be followed by further, two-stage research. (1) Development of a generally acceptable algorithm, determining whether a given thermoanalytical process is controlled by chemical kinetics or by transport processes, which would allow the use of theoretical models belonging to the pertinent family. (2) Development of a new theoretical model, adequate for macrokinetic transport processes of mass- and heat transfer, so that this model can be used, when so indicated, by applying the above algorithm. Such a model should be based on temperature dependance of macro-transport processes, combined with the Clausius–Clapeyron equation.

REFERENCES

1 D. Dollimore, Anal. Chem., 62 (12) (1990) 44R.
2 M. Maciejewski, Thermochim. Acta, 113 (1987) 287.
3 M. Maciejewski and R. Rudnicki, Thermochim. Acta, 113 (1987) 305.
4 M. Maciejewski, J. Therm. Anal., 33 (1987) 1269.
5 M. Maciejewski and J. Baldyga, Thermochim. Acta, 92 (1985) 105.
6 P.D. Garn, Crit. Rev. Anal. Chem., September, 172 (1972) 65.
7 P.D. Garn, Proc. 17th NATAS Conf., NATAS, Rome, GA, 1988, p. 785.
8 W. Kemula and J. Czarnecki, Pol. J. Chem., 52 (1978) 613.
9 T. Flora, Thermochim. Acta, 65 (1983) 113.
10 P.D. Garn, Thermoanalytical Methods of Investigations, Academic Press, New York, 1965.
11 M. Arnold, G. Veress, J. Paulik and F. Paulik, J. Therm. Anal., 17 (1979) 507.
12 J. Šesták, Thermophysical Properties of Solids, Academia, Prague, 1984.
13 J.H. Flynn, Proc. 19th NATAS Conf., NATAS, University Park, PA, 1990, p. 344.
14 J.H. Flynn and L.A. Wall, Polym. Lett., 4 (1966) 191.

15 P.K. Gallagher and D.W. Johnson, Thermochim. Acta, 6 (1973) 67.
16 A.Ya. Rozovskii, Kinetika Topo-Khimitsheskikh Reakcii, Izdatyelstvo Nauka, Moscow, 1974.
17 A.V. Nikolaev and V.A. Logvinenko, J. Therm. Anal., 13 (1978) 253.
18 C. Duval, Inorganic Thermogravimetric Analysis, Elsevier, Amsterdam, 1963.
19 G. Liptay, Atlas of Thermoanalytical Curves, Akademiai Kiado, Budapest, 1975.
20 T. Ozawa, Bull. Chem. Soc. Jpn., 18 (1965) 1881.