THE USE OF COMPLEMENTARY DATA IN THE APPLICATION OF THERMAL ANALYSIS TECHNIQUES

D. DOLLIMORE

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, Lancs., England

Thə use of thermal analytical procedures to obtain both thermodynamic and kinetic parameters is outlined. The advantage of DTA techniques in establishing thermodynamic data is demonstrated. Kinetic data calculated from TG data is demonstrated. Kinetic data calculated from TG data leads to plots of the logarithm of the specific reaction rate constant against $1/T$ (where T is the temperature in degrees Kelvin) and from this point onwards the calculation is the same to establish the kinetic parameters no matter whether the data was obtained from TG or isothermal studies. Information on changes in the density and surface area of solid residues in the decomposition process leads to the conclusion that the number of particles present changes significantly during the decomposition and it is pointed out that this factor is largely ignored in setting up kinetic models for the decomposition of solid materials.

Differential thermal analysis (DTA) and Thermogravimetry (TG) can be used to produce thermodynamic or kinetic data when dealing with the decomposition of solid oxysalts [1]. To obtain unambiguous interpretations however it is necessary to obtain data on the systems under investigations by as many different techniques as possible [2]. The complementary data that can be best utilised are those associated with surface texture and structure [3]. This is especially true when dealing with kinetic aspects of a reaction [4]. In the case of surface properties of the residues left in the decomposition the character of the surface is usually assessed from its adsorption properties. The adsorption usually studied is nitrogen adsorption at the temperature of liquid boiling nitrogen and the interpretation is in terms of the surface area [5] and the pore size distribution [6]. The other important property which changes in a solid state decomposition is the density. This can be combined with the surface area changes to indicate the change in particle size during decomposition [7]. The manner by which the density is determined is important as also is the pretreatment received, such as effective outgassing before commencing measurements [8]. The investigation of solid's receiving heat treatment is made more important in that many industrial processes the solids involved are subjected to a rising temperature programme which can be simulated on DTA or TG equipment. The ancillary information is of two kinds, first information producing kinetic parameters by an alternative route or which restrict the number of possible kinetic processes and secondly data which adds to the general information regarding the

decomposition but which does not necessarily alter the kinetic parameters. First however it must be ascertained that thermodynamic and kinetic data from rising temperature techniques is correctly derived.

Thermodynamic considerations

In reactions of the kind

$$MX(s) \rightleftharpoons M(s) + X(g) \tag{1}$$

the approximate equation:

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T} = \frac{\Delta H}{RT^2} \tag{2}$$

expresses the dependence of the equilibrium pressure of $X(g)$ on the temperature, where R is the gas constant and ΔH is the ordinary heat of reaction at the temperature T. This is of identical form to that which applies to phase equilibrium. The true equilibrium constant K_f is equal to the fugacity (f) of the gas in equilibrium with the solid at a *total pressure* of 1 atmosphere. Strictly it is the variation of $\ln f$ with the temperature which is given by:

$$\frac{\mathrm{d}\ln f}{\mathrm{d}T} = \frac{\Delta H^\circ}{RT^2} \tag{3}$$

where ΔH° is the heat of reaction adjusted to a low value of the total pressure when the gases behave ideally. Experimentally, however, it is the partial pressure p which is measured (equivalent to K_p^1) and in most cases no attempt is made to keep the total pressure at 1 atmosphere, or at a constant value. Although the dissociation pressure should vary to some extent with the total pressure in most experimental cases of thermal decomposition a single gas is liberated and the process consists of noting the equilibrium pressure at each temperature with no attempt being made to keep the total pressure constant. A further assumption is that the activities of the solids also do not vary with pressure. This simple form of the equation is used in several ways. It may be integrated on the assumption that ΔH° is independent of temperature, when

$$\ln p = -\frac{\Delta H^\circ}{RT} + \text{constant} \tag{4}$$

or

$$\log p = -\frac{\Delta H^\circ}{4.567\,T} + \text{constant} \tag{5}$$

when a plot of $\log p$ against $1/T$ should give a linear plot with a slope of $-\Delta H^\circ/4.576$ if ΔH° is in calories.

Alternatively integration between limits gives

$$\ln \frac{P_2}{P_1} = \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 \, T_2} \right) \tag{6}$$

or

$$\log \frac{p_2}{p_1} = \frac{\Delta H^\circ}{4.576} \left(\frac{T_2 - T_1}{T_1 \, T_2} \right) \tag{7}$$

where T_1 and T_2 are the limits of integration with corresponding pressures of p_1 and p_2. If the behaviour is such that ΔH° is not constant with temperature then the above equation can still be applied for small temperature differences ΔT between two adjacent temperature points T_1 and T_2 followed by further calculations for succeeding points.

However in such cases ΔH° can be written as:

$$\Delta H^\circ = \Delta H_0^0 + \Delta \alpha T + \frac{1}{2} \, \Delta \beta T^2 + \frac{1}{3} \, \Delta \gamma T^3 + \ldots \tag{8}$$

when

$$\frac{d\ln p}{dT} = \frac{\Delta H^\circ}{RT^2} + \frac{\Delta \alpha}{RT} + \frac{\Delta \beta}{2R} + \frac{\Delta \gamma T}{3R} + \ldots \tag{9}$$

Integration then gives:

$$\ln p = - \frac{\Delta H_0^0}{RT} + \frac{\Delta \alpha}{R} \ln T + \frac{\Delta \beta T}{2R} + \frac{\Delta \gamma}{6R} \, T^2 + \ldots + I^1 \tag{10}$$

where $\Delta \alpha$, $\Delta \beta$, $\Delta \gamma$ would be constants related to the heat capacities of reactants and the products and I is a constant of integration.

In solid state decompositions however the experimental evidence based on experiments already mentioned provide two different types of behaviour. The first class typified by calcium carbonate produces within the limits of experimental error a linear plot of $\ln p$ against $1/T$. The second class however show no dependence of the value of p upon the temperature. The experimental system normally utilised only enables a single stage of decomposition to be studied. In the first class it needs to be established that the same equilibrium is found in a cooling temperature sequence as in a rising temperature sequence.

Operating the system at a constant temperature and noting the equilibrium pressure is not the only system or the best. The pressure can be set constant and the sample subjected to a rising temperature programme. The sample will then decompose at a temperature which corresponds to the set pressure at which the experiment is run. Furthermore, the total pressure can be set at one atmosphere or other required set total pressure, and the reactant gaseous species [X(g)] set at any required partial pressure and this overcomes the inherent weakness of the traditional system. In principle the DTA or TG units can be operated in this way. In practice the DTA system proves to be the most useful technique to obtain this data but a decision has to be made to decide whether to use the onset temperature of the

peak or the peak temperature as the transition temperature. This can be overcome by desensitizing the DTA equipment to reduce the size of the peak so that the difference between the onset temperature and the peak temperature is so small as to offer no significant difference, when the matter may be formally resolved by noting the peak temperature.

In this way oxides may be dissociated in oxygen/nitrogen mixes with a varying partial pressure of oxygen and a total pressure of 1 atmosphere. Typical investigations of this type concern the DTA investigation of manganese oxides. This demonstrates the further advantage of the DTA method namely that a sequence of dissociations can be studied in a single experiment.

Thus manganese dioxide prepared by the thermal decomposition of manganese nitrate undergoes the following dissociation reactions with the progressive liberation of oxygen,

$$MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO.$$
$$\quad\;\; T_1 \qquad\;\; T_2 \qquad\;\; T_3$$
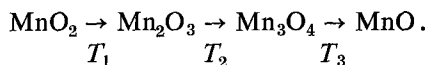
Apart from crystal transformations that may occur the three dissociations noted above may be observed at any stated partial pressure of oxygen such that

$$T_1 < T_2 < T_3 .$$

If the partial pressure of oxygen is now increased then T_1 is increased to $T_1 + \Delta T_1$, and T_2 to $T_2 + \Delta T_2$ etc., so that

$$T_1 + \Delta T_1 < T_2 + \Delta T_2 < T_3 + \Delta T_3$$

and for each transition the relationship

$$\log p = -\frac{\Delta H^\circ}{4.576T} + \text{constant}$$

can be shown to hold with linear plots of $\log p$ against $1/T$.

The system is very usefully employed for the decomposition of carbonates where the pressure of carbon dioxide may be altered or in dehydration reactions where the systems became very complicated. Thus the operation of DTA in this way at various pressures of water vapour may be the only method by which the relationships between the dissociation temperatures and the partial pressure of water vapour may be resolved. The data on carbonates may be qualitatively demonstrated by noting the behaviour of dolomite [Mg Ca $(CO_3)_2$] [11]. At high pressures of carbon dioxide two endotherms are observed, the first peak due to the break down of the dolomite lattice;

$$CaMg(CO_3)_2 \xrightarrow{T_1} CaCO_3 + MgO + CO_2 .$$

At a higher temperature the calcium carbonate decomposes

$$CaCO_3 \xrightarrow{T_2} CaO + CO_2 .$$
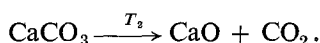
It can quite easily be demonstrated that T_2 will be reduced as the carbon dioxide pressure is reduced but that T_1 remains pressure invariant. Under vacuum conditions the two peaks merge. The behaviour of the first decomposition peak (T_1) under varying pressures of carbon dioxide is simply that the break-down of the dolomite lattice to magnesium carbonate occurs in a region where it is thermodynamically unstable.
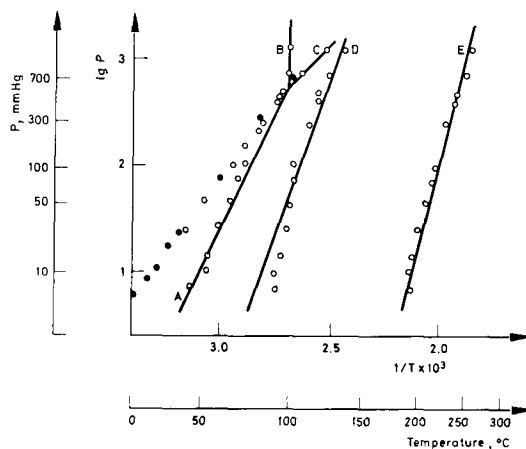

Fig. 1. DTA relationship giving relationship between water-vapour pressure (p) and peak temperature (T) for various stages in the decomposition of $CuSO_4 \cdot 5H_2O$. A. $CuSO_4 \cdot 5H_2O \rightleftarrows$ $\rightleftarrows CuSO_4 \cdot 3H_2O + $ vapour; B. $CuSO_4 \cdot 5H_2O \rightleftarrows CuSO_4 \cdot 3H_2O + $ solution; C. Solution $\rightleftarrows$ $\rightleftarrows CuSO_4 \cdot 3H_2O + $ vapour; D. $CuSO_4 \cdot 3H_2O \rightleftarrows CuSO_4 \cdot H_2O + $ vapour; E. $CuSO_4 \cdot$ $H_2O \rightleftarrows CuSO_4 + $ vapour. Ref. Berg et al .[13].

The variation of transition temperatures in dehydration with the vapour pressure of water above the sample is demonstrated in DTA studies on the dehydration of $Al_2(SO_4)_3 \cdot 16 H_2O \rightarrow Al_2(SO_4)_3 \cdot 14 H_2O \rightarrow Al_2(SO_4)_3 \cdot 12 H_2O \rightarrow Al_2(SO_4)_3 \cdot$ $\cdot 9 H_2O \rightarrow Al_2(SO_4)_3 \cdot 6 H_2O$ [12]. Figure 1 represents the dehydration sequences for $CuSO_4 \cdot 5H_2O$ as represented by Berg et al. [13]. The dehydration of $CoSO_4 \cdot$ $\cdot 7 H_2O$ presents an even more complicated sequence [14]. It is doubtful if such a detailed study of these last two systems could have been made by any other technique.

Kinetic considerations

Technically there is no reason why the traditional kinetic parameters should not be established from rising temperature experiments.

$$\frac{d\alpha}{dt} = kf(\alpha) \qquad (11)$$

where $\dfrac{d\alpha}{dt}$ is the rate of decomposition, α is the fraction decomposed, t is the time and $f(\alpha)$ is the function of α which fits the isothermal decomposition process. The rate constant is then k. The variation of the specific rate constant with temperature is given by the Arrhenius equation

$$k = A\,e^{-E/RT}. \tag{12}$$

It is assumed that the rate constants in these two equations are identical. Finally the relationship between time (t) and temperature (T) is

$$T = T_0 + bt \tag{13}$$

where T_0 is the temperature at $t = 0$, and b is the heating rate. It is usual to combine all three equations but this obscures several valuable points.

The combination of the first and last of these equations gives:

$$k = \frac{\dfrac{d\alpha}{dT} \cdot b}{f(\alpha)}. \tag{14}$$

This will produce values of k at each temperature so that a plot of log k against $\dfrac{1}{T}$ can be constructed and from this point on the treatment is similar irrespective of whether k was calculated from isothermal or rising temperature data. The published treatments of rising temperature methods all utilise a combination of the three equations. [15]

But the resultant equation

$$\log\left[\frac{\dfrac{d\alpha}{dt}}{f(\alpha)}\right] = \log\frac{A}{b} - \frac{E}{Rt} \tag{15}$$

may not provide as much information as the previous expression giving k and enables the conventional plot of log k against T to be constructed. If this plot is not linear then three reasons for this have to be considered, namely

    1. The incorrect form of $f(\alpha)$ has been choosen
    2. The Arrhenius equation does not describe the temperature dependent behaviour of the kinetic parameters
or 3. The specific rate constant in the Arrhenius equation is not identical with the rate constant in the kinetic equation
 $\dfrac{d\alpha}{dt} = kf(\alpha).$

In published work the Arrhenius equation is assumed, and the concentration of efforts is on the selection of the correct function $f(\alpha)$. Furthermore great emphasis

is placed on the calculation of E with little attention being paid to the evaluation of A. Even if however the significance of these parameters is merely empirical it is still necessary to calculate both to enable the system to be completely described.

Ancillary information regarding texture of solid residue

These are various measurements which may be made which help to describe the changes taking place during the thermal decomposition of a solid subjected to a rising temperature programme. In particularly methods which provide information regarding the surface or volume changes of the solid residues from decomposition are important in assessing probable kinetic functions which are largely based on geometry considerations regarding the reaction interface. It must be emphasised here however that there is quite a clear distinction between the reaction interface and the surface texture or surface area except in the special case represented by total gasification of the solid phase reactant, i. e.

$$A(s) + B(g) \rightarrow AB(g)$$
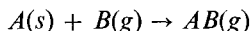
In this study two properties of the solid residue are discussed, namely the surface area as determined from adsorption experiments and the density changes which occur as the decomposition progresses.

The general reaction considered already, namely

$$MX(s) \rightarrow M(S) + X(g)$$
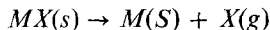
will produce a reaction interface which might be based solely on geometric considerations but for the fact that these are changes in volume due to differences in density between oxysalts and their corresponding oxides which will cause a distortion of the simple geometric shape of the interface. Finally there will be a break up of the original particles under the strain imposed by these differences in volume [16, 17].

Let the starting material (MX) consist of N_1 particles per mole with a molar volume and molar surface area of V_1 and S_1 respectively. The molar volume of the starting material is given by:

$$V_1 = \frac{M_1}{P_1} = \frac{4}{3} \pi N_1 r_1^3 \tag{16}$$

where M_1 is the molecular weight in grammes, P is the density, and r is the average radius of the particles considered as spherical. The molar surface area of the original material is:

$$S_1 = s_1 M_1 = 4 \pi N_1 r_1^2 \tag{17}$$

where s_1 is the experimental surface area in $m^2 g^{-1}$.

From (16) and (17)

$$r_1 = \frac{3 V_1}{S_1} = \left(\frac{S_1}{4 \pi N_1} \right)^{1/2} \tag{18}$$

If, in decomposition, all that occurs is an alteration in the size of each particle due to alterations in the molar volume of the solid produced, then the mean radius r_2 of the product is given by:

$$r_2 = \frac{3V_2}{S_2} = \left(\frac{S_2}{4\pi N_1}\right)^{1/2}$$

(19)

where the subscripts 2 refer to the product, but the number of particles produced remains the same and is therefore written as before, as N_1.
Then:

$$\frac{V_1}{V_2} = \left(\frac{S_1}{S_2}\right)^{3,2}$$

(20)

One can examine systems to check on this particular equation. Thus a sample of barium oxalate upon decomposition gave the data shown in Table 1.

Table 1

Decomposition data on barium oxalate ($BaC_2O_4 \cdot 1/2\ H_2O$) heated for 1/2 hour at indicated temperature in air.

Tempera-ture, °C	Wt. loss, %	Density of solid residue, g cm^{-3}	Observations
100	0	1.866	Specific surface area 0.5 mg$^{2-1}$
210	4.0	1.92	Dehydration
308	4.3	2.06	
402	4.4	2.15	Specific surface area 3.1 mg$^{2-1}$
460	12.0	2.70	Specific surface area 8.4 mg$^{2-1}$
495	15.6	3.74	Decomposition to $\gamma BaCO_3$
556	15.9	4.18	
655	16.0	4.89	Specific surface area 9.7 mg$^{2-1}$
745	16.1	4.52	
800	16.1	4.40	
860	16.1	4.54	Possibly due to transition to
900	16.1	4.39	to $\beta BaCO_3$

Samples weighing 0.5 g used in each experiment.
    Ref. 17.

In going from barium oxalate to barium carbonate the ratio V_1/V_2 is 2.597, whilst the corresponding value of $(S_1/S_2)^{3/2}$ is 0.2204. This discrepancy with the formula is due to the change in volume on going from barium oxalate to barium carbonate causing strain to be set up in the system which causes the original particles to shatter into a number of smaller particles. If the number of product particles (in this case barium carbonate) was N_2, then:

$$r_2 = \frac{3V_2}{S_2} = \left(\frac{S_2}{4\pi N_2}\right)^{1/2}$$

(21)

The ratio V_1/V_2 is then:

$$\frac{V_1}{V_2} = \left(\frac{S_1}{S_2}\right)^{3/2}\left(\frac{N_2}{N_1}\right)^{\frac{1}{2}} = \left(\frac{S_1}{S_2}\right)^{3/2} N^{1/2} \tag{22}$$

where N is the number of particles formed from a single reactant particle.

Possibly the only cases where Eq. (20) is found are either where the change in molar volume of reactant and product is relatively small or where the loss of the
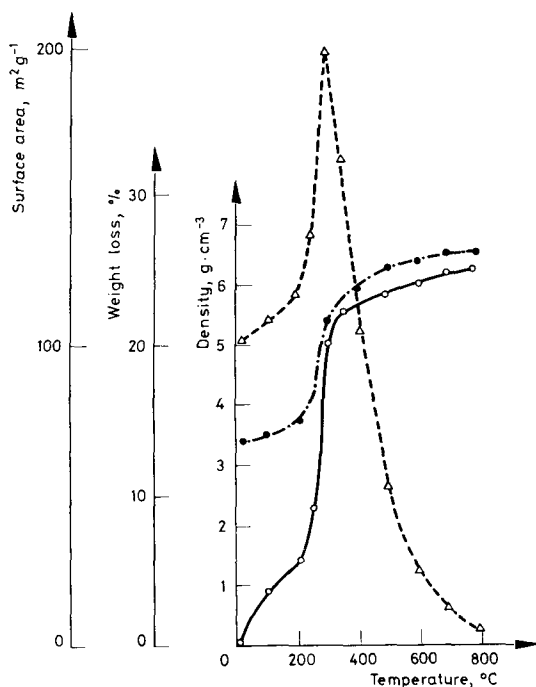

Fig. 2. Density, surface area and % weight loss on solid residues from heat treatment of nickel hydroxide. Ref. 16. — △ — — Surface area; ●·—● Density; —○—○— wt. loss. %

gaseous product is by channelling, leaving an open network of narrow pores as in the dehydration of zeolites. The use of Eq. (22) may be illustrated by data published by Dollimore and Pearce [16] on nickel hydroxide. Figure 2 gives experimental data from which the calculations can be made. Figure 3 shows the application of this data to nickel hydroxide and similar data for nickel carbonate also studied by Dollimore and Pearce. Table 2 summarizes the data of these authors taken from the maximum point of surface area for this and similar data on other nickel salts.

Table 2

Estimate of the number of particles formed from a single particle of original material.

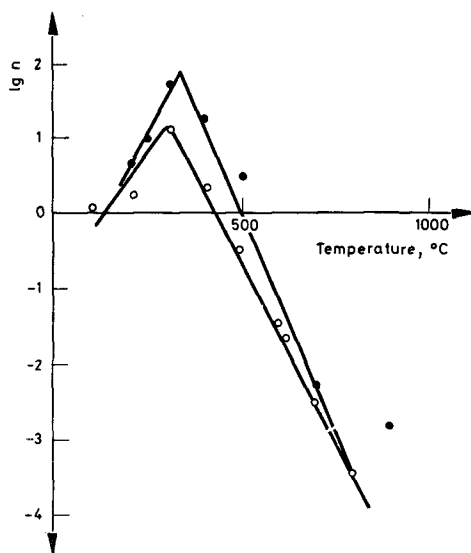| Nickel salt	n	Surface area, per g of material	Surface area, per g of oxide	Temperature, °C
Nitrate	75.131	37.0	37.0	400
Ammonium nitrate	38.967	32.5	33.1	345
Acetate	1342	58.9	61.62	300
Sulphate	2.83	69.8	120.7	200
Carbonate	50.0	239	260	300
Hydroxide	15.05	201	214	300

Ref. 16.

Fig. 3. Logarithmic relation between number of product particles formed from a single particle of original material and temperature of treatment. Nickel hydroxide and nickel carbonate. Nickel carbonate ●—●—●; Nickel hydroxide —○—○—

In making the calculations on these partially decomposed samples the effective molecular weight of the partially reacted material (M_2) is estimated by the use of the formula,

$$M_2 = (1 - \alpha)M_1 + \alpha M_3.$$

where M_3 is the molecular weight of the product and α is the fraction decomposed (at $\alpha = 1$, $M_2 = M_3$). The general pattern of an increase in the number of particles upon decomposition is observed, together with a coalescence or sintering of particles upon heat treatment with no decomposition or after decomposition has occurred.

These observations have a profound implication upon the theories that relate decomposition kinetics to theoretical models. These theoretical models are all built up on the idea of a reaction interface which changes in total area but with a system in which no alteration in the number of particles in the system is contemplated. The data presented here shows quite clearly that as well as a changing reaction interface within each particle there is also a change in the number of particles during solid state decompositions. No existing model for kinetic processes dependent upon a reaction interface in solid state decompositions adequately deal with this clearly demonstrated phenomena. The nearest approach is that of Komatsu [18] in which a spread of the reaction interface from one particle to another is postulated via the points of contact between them.

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RÉSUMÉ — On donne un aperçu sur l'utilisation des procédés thermoanalytiques en vue d'obtenir les paramètres thermodynamiques et cinétiques. On montre les avantages des techniques d'ATD pour établir les données thermodynamiques. Les données cinétiques calculées à partir des courbes TG conduisent au tracé du logarithme de la constante spécifique de vitesse de réaction en fonction de 1/T, T étant la température en degrés Kelvin. A partir de là, le calcul pour établir les paramètres cinétiques est le même, que les données aient été obtenues par TG dynamique ou isotherme. Les données relatives aux changements de densité et de surface spécifique des résidus solides au cours des réactions de décomposition permettent de conclure que le nombre de particules présentes change d'une façon importante pendant la décomposition. On insiste sur ce fait qui reste souvent négligé lors de l'établissement des modèles cinétiques de décomposition des matériaux solides.

ZUSAMMENFASSUNG — Der Einsatz thermoanalytischer Verfahren zur Bestimmung sowohl thermodynamischer als auch kinetischer Parameter wird beschrieben. Der Vorteil der DTA-Techniken bei der Ermittlung thermodynamischer Daten wird gezeigt. Die aus TG-Daten berechneten kinetischen Daten führen zu graphischen Darstellungen der Funktion des Logarithmus des spezifischen Reaktionsgeschwindigkeitskonstante gegen 1/T (wobei T die Temperatur in Kelvin bedeutet). Hiervon ausgehend ist die Berechnung der kinetischen Parameter dieselbe, ungeachtet dessen, ob die Daten aus TG-Messungen oder aus isothermen Untersuchungen erhalten worden waren. Die Information bezüglich der Änderungen der Dichte und Oberfläche fester Rückstände von Zersetzungsprozessen führt zu der Folgerung, daß die Zahl der anwesenden Teilchen sich während der Zersetzung wesentlich ändert. Es wird betont, daß dieser Faktor bei der Entwicklung zur Zersetzung von Festkörpern in vielen Fällen ausser Acht gelassen wird.

Резюме — В общих чертах описано использование термических аналитических методов для получения как термодинамических, так и кинетических параметров. Показано преимущество методов ДТА при установлении термодинамических данных. Кинетические данные, вычисленные из данных ТГ, приводят к графикам в координатах логарифм удельной реакционной константы скорости и 1/T (где T — температура в градусах Кельвина) и с этой точки зрения дальшие вычисления те же самые для установления кинетических параметров, независимо от того, что данные получены из ТГ или изотермических исследований. Информация об изменениях плотности и площади поверхности твердых остатков в процессе разложения приводит к заключению, что число частиц заметно изменяется во время разложения и показано, чро этот фактор в большинстве игнорируется при установлении кинетических моделей разложения твердых материалов.