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FATCORS INFLUENCING THERMOANALYTICAL CURVES

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The experimental conditions influencing thermoanalytical results are summarized and subdivided into three groups: sample properties, experimental parameters, apparative parameters. By means of selected examples, some experimental conditions are discussed, mainly for TG and DTA. Special care is given to particle size, the atmosphere as part of the reacting system and as experimental parameter, the buoyancy problem, dynamic re-impact phenomena of molecules, heat transfer and supercooling problems in melting, and DTA under different isobaric conditions. In quantitative thermal analysis, experimental conditions need careful control. Standard reference materials as well as automatic data collection and processing techniques help in achieving better thermoanalytical results.

In contemporary thermal analysis an increasing trend towards quantitative applications of its methods to various branches of natural sciences is becoming evident, e.g. to physical and inorganic chemistry. This is due not only to the present availability of highly-elaborate, accurate and reliable thermal analytical laboratory equipment, but also to the fact that an ever larger number of scientists are becoming aware of the wide capacities, elegancy and speed of these techniques (see e.g. Oswald and Dubler [1]).

Considering thermoanalytical results with regard to their quantitative significance, it has to be recognized that much of the information obtained is of an empirical nature in that it depends on a number of experimental conditions. Therefore parameters such as furnace heating rate, geometry of sample holder and furnace, sample container material and shape, as well as amount, volume, particle size, packing and thermal conductivity of sample, etc. tend to be difficult to reproduce in part and thus have to be given great attention. Equally, the atmosphere around the sample needs careful consideration and control. The particular importance of the experimental conditions in thermal analysis is stressed by the trivial consideration that in other current investigations of chemical reactions, e.g. titrations or synthetical work, many important parameters such as the concentration of the reactants, temperature, etc. can be influenced to a wide extent during the entire course of the process, whereas in thermal analysis the experiment is carefully prepared, e.g. by mixing the components of a reaction between two solids, loading

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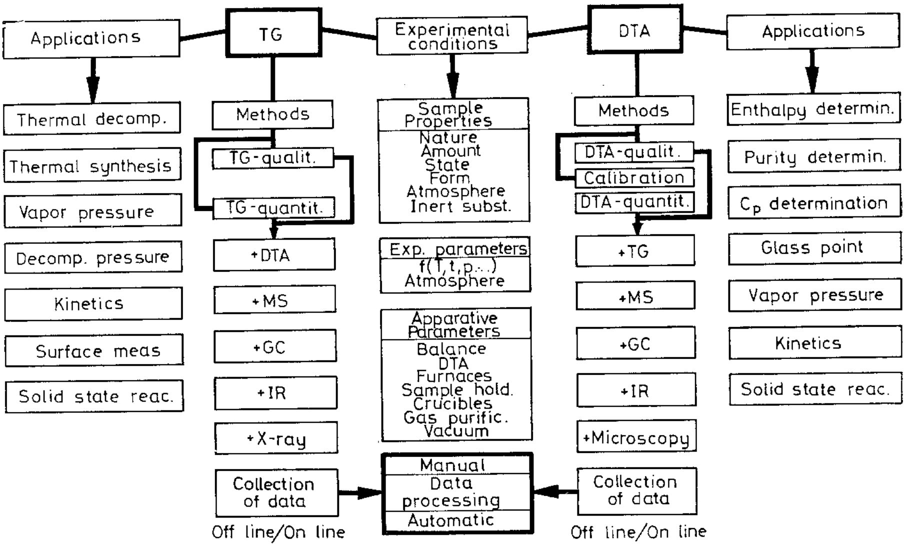

Fig. 1. Experimental conditions in quantitative applications of thermoanalytical methods

the balance, setting the temperature program and reaching the desired vacuum, but can then no longer be varied after it has once been started.

In Fig. 1, a survey of quantitative applications of TG and DTA, both alone and combined with other techniques, is given. The central region comprises a choice of important experimental conditions, which are further subdivided into the three groups "sample properties", "experimental parameters", and "apparative parameters". A few of these factors, including some less common ones, will be treated in more detail, first for TG and then for DTA, although completeness lies far beyond the scope of this article.

Some experimental conditions in thermogravimetry

Among the sample properties, the nature of the particular specimen of a substance under investigation may very significantly influence its thermoanalytical behaviour, as the variability of solids, although of equal chemical composition and crystal structure, is almost infinite. This is a direct consequence of the real lattice structure of crystalline solids, comprising all the influences of, e. g., point defects, dislocations, grain and subgrain boundaries. For fine powders, additional effects of porosity and particular surface properties have to be taken into account. As an example among many others, the characteristically different TG curves for thermal decomposition of hydrozincite, $Zn_5(OH)_6(CO_3)_2$, may be cited, which have been measured by Wiedemann [2, 3] on a very sensitive scale for equal amounts of samples from various natural origins and artificial preparation procedures. Frequently, the "history" of a sample is reflected in its thermal analytical behaviour. It is often difficult, however, to give full explanations for such phenomena on a microscopical basis.

With respect to the weights of samples, the authors would like to restrict themselves here to the statement that, for a number of reasons, small enough probe weights or sample volumes should be used. In the study of average thermal decomposition reactions, sample weights of the order of about 10 mg are considered well adequate today. The factor of the sample weight becomes particularly critical if reliable knowledge in the field of solid-state kinetics and mechanisms is aimed at.

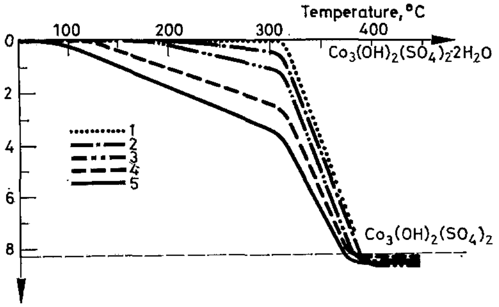

Fig. 2. Influence of particle size on the dehydration of $Co_3(OH)_2(SO_4)_2 \cdot 2\,H_2O$. 1: 250 μm, 2: 100 μm, 3: 10μm, 4: 1 μm, 5: 0.3 μm (samples of 10 mg, heating rate 6°/min, nitrogen atmosphere 5 l/h)

Of further importance is the state and form of samples. Work on the influence of particle size on thermoanalytical results has been published, for example, by Barrall and Rogers [4], who state that a packing of fine particles has better thermal conducting properties than an arrangement of coarse grains, and by Bayliss [5]. As an example, the TG curves for the dehydration of 6 mg of either single-crystalline or powdered whewellite, i. e. natural $CaC_2O_4 \cdot H_2O$, in high vacuum may be considered, as measured by Wiedemann [6] and shown in Fig. 10 below. The pronounced difference in the curves – particularly at higher heating rates – illustrates the marked effect of particle size which, in this case, cannot be explained only by a difference in the thermal conductivities of the samples. For the same phenomenon a detailed study has been carried out by Dubler and Oswald [7, 8] on the first dehydration step of a cobalt hydroxy-sulphate hydrate, $Co_3(OH)_2(SO_4)_2 \cdot 2\,H_2O$, which releases both crystal water molecules in one step between 100 and 380°, leading to a net plateau for $Co_3(OH)_2(SO_4)_2$. This reaction was investigated by TG on five crystalline 10 mg samples of different, uniform, carefully characterized particle sizes between 0.3 and 250 μm. Figure 2 shows a very strong dependence of the onset temperature of the reaction on particle size, whereas the temperatures of maximum reaction rate as found by DTG and of the end of the dehydration are much less influenced. With 0.3 μm particles the reaction already starts from 85°, compared to 310° for 250 μm crystallites. The detailed kinetical investigation using different mathematical approaches agrees on a significant mechanistic change around 305°. In the region between 120 and 280°, it was concluded that for the 0.3 μm particles the nucleation of the product phase with an activation energy of 4.2 kcal/mole might act as the rate-determining step, whereas for a medium particle size of 10 μm, the activation energy of 13.0 kcal/mole points to control by the diffusion of water molecules through still intact regions of the initial lattice. For the range above 305°, the activation energy is much higher, but little can be said at present about the detailed mechanism of this step. In order to understand such complex reactions fully, crystal structural relationships between the phases involved, i. e. topochemical or topotactic viewpoints, seem to be very important.

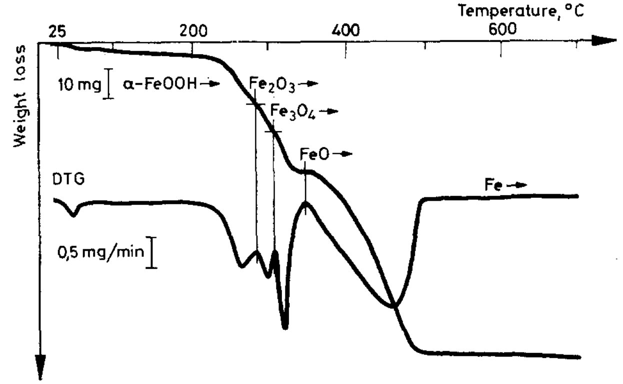

Fig. 3. TG and DTG curves for the reaction of α-FeOOH in 99.9% molecular hydrogen (sample weight 265 mg, heating rate 4°/min)

Why has the atmosphere been listed in Fig. 1 among the sample properties? Because, besides its nature as an experimental parameter, in many cases it can also be a part of the sample system, i.e. a reactant of the chemical process under consideration. As one of a vast number of examples, the stability relations in the iron–iron oxide system as a function of temperature and oxygen partial pressure in the atmosphere as described by Peters and Möbius [9] may be considered (for the original data see Mann [10]), which holds, via Boudouard- and carbon dioxide thermal dissociation-equilibria, for CO/CO_2 mixtures as well. If, for example, a TG recording of a sample of α-FeOOH in a reacting atmosphere of 99.9% pure molecular hydrogen is started from room temperature, the DTG curve in Fig. 3 demonstrates particularly well how, after the release of slight amounts of adsorbed water, the oxide phases α-Fe_2O_3, Fe_3O_4 and FeO are subsequently formed, before metallic iron is obtained as a final product.

Interesting influences of a reacting component from the atmosphere can also be observed when gypsum ($CaSO_4 \cdot 2\,H_2O$) is thermally decomposed at various water vapor partial pressures, as reported e.g. by Kuntze [11], Fowler [12], or Wiedemann and Bayer [13]. For the experiment shown in Fig. 4, drawn from ref. [13], cleavage plates of natural selenite of identical size and weight (10 mg) were submitted to a linear heating and subsequent cooling program at a rate of

2°/min. Heating in static or flowing air atmosphere at 20 torr water vapor partial pressure leads directly to γ-anhydrite. During cooling, rehydration to the hemihydrate occurs due to the water vapor content of the air. The other two TG curves show the effects of higher water vapor pressures on the dehydration. Under these conditions the heating curves are characteristically influenced by the intermediate formation of the hemihydrate. The curve at $p_{H_2O} = 120$ torr shows initially the superposition of the two effects, the dehydration to anhydrite and the back-diffusion of water which favours the formation of the hemihydrate, leading to a small intermediate maximum at 153°. At 600 torr water vapor pressure there appears a corresponding shoulder in the heating curve at 184°. The reversible reaction hemihydrate $\leftrightarrows$ γ-anhydrite is topochemical or, more precisely, topotactic (cf. Günter and Oswald [14]) in nature, similar structural elements being present in both crystal lattices. There is a high degree of mobility of water molecules between $CaSO_4$ layers, explaining the particular ease of rehydration of γ-anhydrite to the hemihydrate.

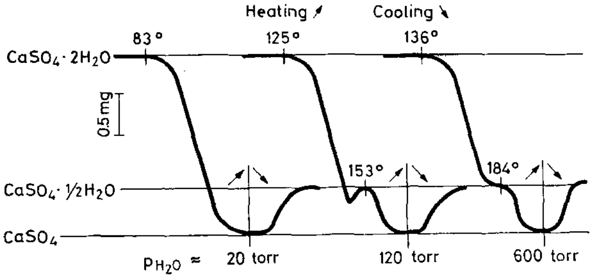

Fig. 4. Decomposition of natural gypsum crystals and rehydration of γ-anhydrite to hemihydrate at different water vapor pressures (samples of 10 mg, heating/cooling rate 2°/min).

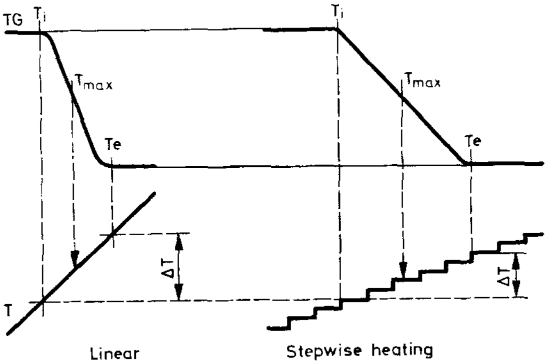

Fig. 5. Schematical presentation of the dependence of a slow thermal dissociation reaction on the heating schedule

Passing to specific experimental parameters, the temperature will be discussed first. The heating rate is important in so far as the programmed raise in temperature often tends to precede the course of the reaction under study, particularly if the latter proceeds slowly. To overcome this, the usual linear heating program may be replaced by a stepwise one, approaching more the isothermal conditions. Figure 5 shows schematically the effects of stepwise heating, namely a smaller interval ΔT between T_i (initial) and T_e (end), as well as a shift in the temperature of maximum reaction rate, T_{max}, in comparison to a linear heating process. By such measures it is also possible to obtain reliable thermodynamic data by dynamic, thermoanalytical methods. This has been demonstrated, for example, by Bayer and Wiedemann [15], who, by careful stepwise heating in the thermal dissociation reaction $2\,PdO \leftrightarrows 2\,Pd + O_2$, measured a straight line for the dependence of $1/T_{max}$ on the oxygen pressure, which approximates almost perfectly to the thermodynamic equilibrium line determined by other authors using static methods. It is not likely that such an agreement could have been attained with the usual linear heating. Further systems which have been investigated in a similar way by stepwise heating procedures are BaO_2-BaO [16], and calcite and dolomite [17]. In the same context, attention must be drawn to the work by Paulik and Paulik [18, 19] about the careful study of decomposition reactions under "quasi-isothermal" (and "quasi-isobaric") conditions. Their method aims equally at an elimination of pernicious gas- and heat-transfer processes in order to provide the possibility of studying decomposition reactions in a more thorough way.

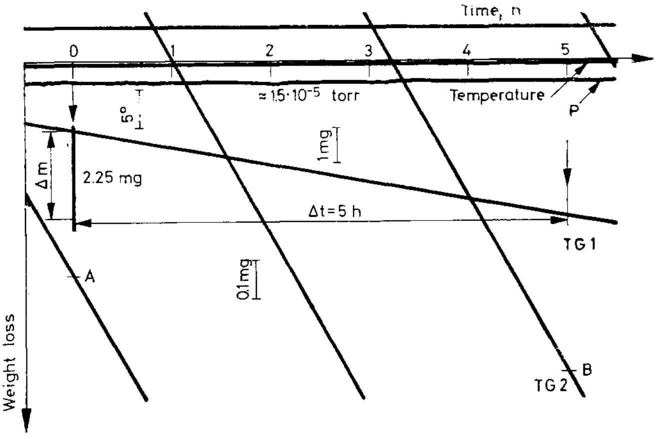

Fig. 6. Original diagram of a vapor pressure measurement weight loss produced by effusion of benzoic acid vapor from a Knudsen cell through a calibrated orifice ($7.147 \cdot 10^{-3}$ cm^2) under isothermal conditions (17.25°), recorded as a function of time simultaneously with sample temperature and pressure outside the cell

For an illustration of the experimental parameter of time, the evaporation of a volatile substance through the small orifice of a Knudsen effusion cell housed on a thermobalance at constant temperature and pressure, leading to applications of thermogravimetry for vapor pressure determination, is discussed. Such experiments have been undertaken previously by Motzfeldt [20] in the field of high-temperature vapor pressure measurements on inorganic substances, as well as by Cordes and Schreiner [21] for organometallic complexes. The original curve shown in Fig. 6 was produced by Wiedemann [22] and concerns the effusion of benzoic acid vapor from the cell through a calibrated orifice under isothermal conditions (17.25°), recorded as a function of time simultaneously with sample temperature and pressure (1.5×10^{-5} torr) outside the cell. The two weight traces, recorded at different sensitivities, show a constant rate of weight loss. In total, 2.25 mg of benzoic acid effused within 5 h, corresponding to an effusion rate of $\sim 10^{-7}$ g · sec^{-1}. The vacuum outside the effusion cell should be about one order of magnitude better than the vapor pressure to be determined. A cold trap near the orifice of the Knudsen cell serves to condense the vaporized compound and assists in stabilizing the external pressure. With the available instrumentation, this measurement technique is applicable over the pressure range from 1 to 10^{-6} torr. By simple calculations, it yields vapor pressure and volatilization enthalphy results within comparatively little time. Evidently, a number of experimental conditions, such as the sensitivity and reproducibility of the balance, as well as the temperature of the sample and the effusion cell, are very critical. For a test lasting 10 to 20 h, the maximum drift of the balance should not exceed ± 5 μg, and the temperature should remain constant within about $\pm 0.1°$.

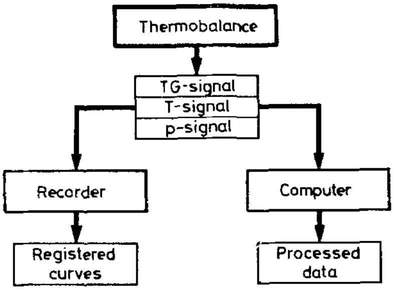

Fig. 7. On-line data processing for thermogravimetric vapor pressure determination

In connexion with the thermogravimetric vapor pressure determination, the possibility of fully automatic collection and evaluation of thermoanalytical data has to be mentioned. Essentially, it is possible to realize every desired quantitative evaluation procedure in thermal analysis by means of a suitable interface and a computer. In fact, such automatic methods for collecting and processing high numbers of measured values can be considered as particularly adequate for a clearer recognition and quantification of factors influencing thermal analytical results. As an example, the on-line data processing for vapor pressure determination by thermogravimetry is schematically presented in Fig. 7. The four subsequent steps in the evaluation of the respective results are listed in Table 1, which has been in part directly copied from the computer output. Another method for the determination of vapor pressure, namely by DTA and applicable for pressures up to 760 torr, will be mentioned later.

Table 1 Computerized evaluation of vapor pressure from thermogravimetric measurements

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Registered Curves

Visual control of the proceeding experiment, distinct documentation of the data outprint

Processed Data

Step 1

The weight (TG), temperature (T) and pressure (p) signals are collected per time unit and used for the evaluation of standard deviations. These results of measurements at different temperatures are used for the next step, if the linearity of evaporation is proved.

Statements:
- linear evaporation means a pure substance
- positive deviation from linear evaporation can be due, for example, to association of molecules or atoms or to lack of substance
- negative deviation from linearity can be caused, for example, by dissociation of the investigated compound
- impurities may lead to deviations in either positive or negative direction

Variations smaller than $\pm 5\%$ in the pressure outside the Knudsen cell are not critical.

Step 2

Input of collected data for vapor pressure calculation

- rate of evaporation $= \frac{\Delta m}{\Delta t}$ [g · sec^{-1}]
- temperature T
- orifice area Q

$$\Delta P_s = \frac{\Delta m}{\Delta t} \cdot \frac{1}{Q} \cdot \sqrt{\frac{2RT}{M}} \quad [\text{dyne} \cdot \text{cm}^{-2}]$$

Constant pressure outside Knudsen cell $p \sim 1.5 \times 10^{-5}$ torr

Data Input — Vapor Pressure Benzoic Acid BDH

122.12 Molecular Weight M

Number of measurement	Temperature, deg C	Rate, g/sec	Orifice Q, cm^2
1	17.25	1.25×10^{-7}	0.007147
2	21.25	2.25×10^{-7}	0.007147
3	25.15	3.20×10^{-7}	0.007147
4	26.65	3.89×10^{-7}	0.007147
5	27.35	4.59×10^{-7}	0.007147
6	31.25	6.67×10^{-7}	0.007147
7	42.35	2.28×10^{-6}	0.007147

Table 1 (cont.)

Step 3

Output of the calculated vapor pressure

Regression Analysis of Vapor Pressure Data

Measured values		Calculated values		
T, deg C	P, torr	T, deg K	1000/T	log10 P
17.25	0.00046	290.41	3.44341	−3.32209
21.25	0.00084	294.41	3.39662	−3.10608
25.15	0.00120	298.31	3.35222	−2.90106
26.65	0.00146	299.81	3.33545	−2.82363
27.35	0.00172	300.51	3.32768	−2.78775
31.25	0.00252	304.41	3.28504	−2.59092
42.35	0.00878	315.51	3.16947	−2.05732

Output Vapor Pressure Benzoic Acid BDH

Function: $\log(P) = A \times 1000/T + B$

Coefficients		Deviations	
A	B	Average	Maximum
−4.6170	12.5762	0.017822	0.028627

Step 4

Output of evaluated thermodynamic data

Thermodynamic Properties

$\Delta H_s(T_0)$, kcal/mole	$\Delta S_s(T_0$, 760 torr), cal/mole·deg K
21.1114 ±0.3815	44.3311 ±1.2703

(Standard Reference State $T_0 = 302.97$ deg K)

ΔH_s Enthalpy, ΔS_s Entropy } of Sublimation

The atmosphere and pressure – as experimental parameters now – are of general importance as they may in principle allow or not allow a given reaction at a given temperature. Instead of entering deeper into this matter, a problem will be touched upon which connects the atmosphere and the apparative parameter "balance", i. e. the buoyancy effect. This is often neglected, but if high accuracy is requested, this is not justifiable. An early treatment of the correction for the influence of buoyancy was given by Simons et al. [23]. Against the proposal to introduce the necessary corrections quite generally in data evaluation programs, it can be said that besides the buoyancy effect for well-known parts of the balance system and crucible, there is also the buoyancy of the sample itself, which changes during the experiment in weight and density, and the contribution of the surrounding atmosphere, which may not be constant either. As an example of the extent of buoyancy influences and corrections, the initial and final parts in the TG recording from the decomposition of a particularly large sample of nearly 2 g $CaCO_3$ in a CO_2 atmosphere are discussed by means of Fig. 8, drawn from a paper by Peters and Wiedemann [24]. This investigation was undertaken in order to test

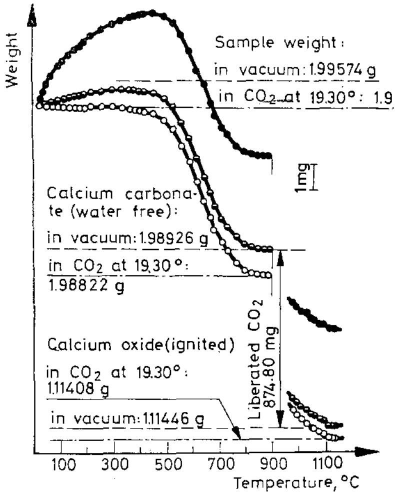


Fig. 8. Thermal decomposition curve of $CaCO_3$ in CO_2 atmosphere. The curve parts above 900° are shifted upwards for 870 mg. –●–●–●– uncorrected weight; –◒–◒–◒– correction for the change of buoyancy of crucible and crucible holder system with temperature applied; –○–○–○– additional correction for the change of sample buoyancy applied. Weight in CO_2 at temperature of the balance (19.30°)

the accuracy of a thermobalance, and a CO_2 atmosphere had to be chosen because the otherwise very pure precipitated $CaCO_3$ exhibited a small weight decrease of about 0.3% – probably due to the loss of strongly adherent water – between 400 and 800°. As the thermal liberation of CO_2 started in air from 700°, but in CO_2 at 895° only, an overlap of the two effects could be avoided by using a CO_2 atmosphere. Besides the actually measured uncorrected weight curve, a second one is shown for which a correction for the buoyancy influence of the crucible and crucible holder system as a function of temperature is applied, and a third one, where in addition the buoyancy change of the sample is also taken into account. Moreover, the exact sample weights at room temperature, after the loss of adsorbed water at 800°, and at the end of the experiment at 1100°, ~~are~~ indicated both for CO_2 at 19.30° (temperature of the balance) and corrected for vacuum. The extents of the corrections are clearly visible in Fig. 8. From the weights of dry $CaCO_3$ and CaO it is possible to calculate the atomic weight W of Ca by this experiment. If direct, uncorrected weights are used, a weight loss due to adsorbed water of 1.83 mg and $W = 40.273$ are determined, whereas from the weights corrected for vacuum the corresponding results are 6.48 mg and $W = 40.067 \pm 0.01$, to be compared to $W = 40.08$ approved by the IUPAC in 1971. The average error of a single weighing is ± 0.08 mg. From this example it becomes evident that accurate results are obtained only with consideration of the buoyancy contributions of the sample, the crucible and the crucible holder, all dependent on temperature.

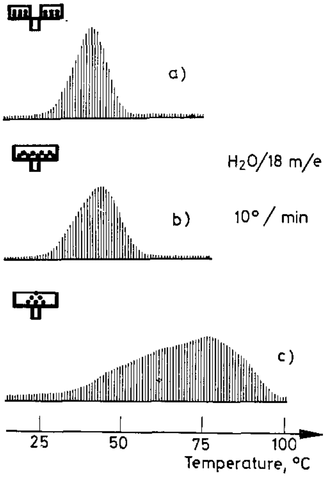


Fig. 9. Influence of different kinds of sample packing in the holder, demonstrated with calcium oxalate monohydrate. The profiles a—c represent water vapor pressures recorded by mass-spectrometry during thermal dehydration (sample weight 7 mg, starting pressure $5 \cdot 10^{-5}$ torr, heating rate 10°/min, grain size 150 mesh)

At higher temperatures, the approximately parabolic buoyancy correction curve can become further complicated by a marked increase starting from about 700°. Wiedemann [25] has shown that this effect is caused by thermal radiation or convection, leading to a heating of parts of the balance system, and that it can be avoided by insertion of an intense cooling between the furnace and the adjacent balance housing. Duval [26] has tried to preserve the balance from heat radiation by a special mechanical shielding device.

As regards the parameter "furnace", it is inevitable that there always exist distinct radial and vertical temperature gradients which should be established by calibration. For an example, reference may be made to the determination of the vertical temperature distribution shown by Wiedemann [27]. In addition, however, the amount and shape of sample can induce a temperature gradient – a fact of particular importance in kinetic measurements. Considerable temperature differences can also be present in practice at different sites of one and the same sample holder; in distinct cases differences of several degrees have been measured. Of course, the thermal conductivity of sample holder and crucible materials, such as Pt, Au, Al_2O_3 or quartz, is an important parameter. Details about the temperature distribution in furnaces may be derived from experiments with specially designed multiple-sample holders, where equal fractions of the substance are housed in several, symmetrically arranged small pans.

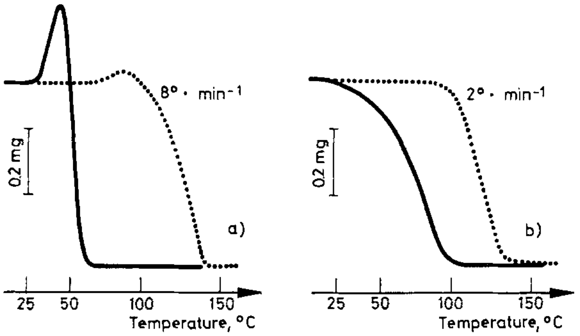


Fig. 10. Dehydration of whewellite ($CaC_2O_4 \cdot H_2O$). Solid line, powdered material (particle size 150 mesh); dotted line, single crystal (ca. 1×1×2 mm); every sample weight 6 mg, initial pressure 10^{-5} torr a) heating rate 8°/min; b) heating rate 2°/min

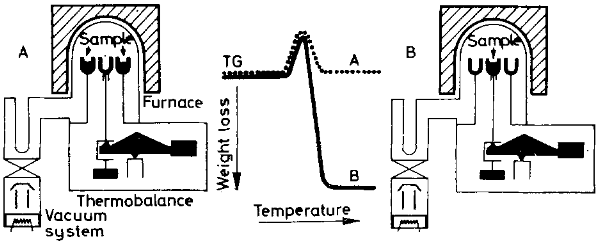


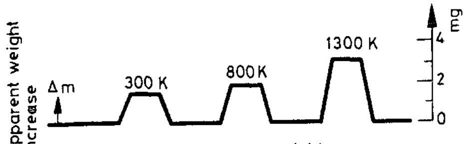
Fig. 11. Dehydration of whewellite ($CaC_2O_4 \cdot H_2O$). Powdered material (particle size 150 mesh); sample weight 6 mg, heating rate 8°/min, initial pressure 10^{-5} torr. A) dotted line, weight change during reaction in a ring with substance housed beside the empty balance crucible; B) solid line, weight change during reaction with substance housed on the balance crucible

Moreover, the arrangement of the substance on the sample holder is very important. This was illustrated, for instance, by means of simultaneous TG–DTA measurements in connexion with gas-analytical investigations by Wiedemann [28]. The three profiles shown in Fig. 9 represent water vapor pressures recorded with the mass-spectrometer during thermal dehydration of fine-grained calcium oxalate monohydrate. Whereas arrangements a) and b) lead to rather similar, almost symmetrical peaks with rapid dehydration, completion of the reaction is much delayed in case of c), leading to a shift in the peak maximum of almost 40°. For investigations in vacuum the layer of the substance in the crucible should be kept as thin as possible, not exceeding 0.5 to 1 mm.

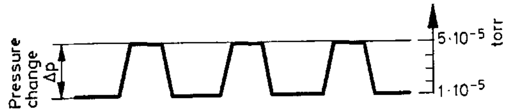
Under the keyword "vacuum" in apparative parameters, an interesting case of apparent weight gain of a sample during its heating will be discussed, as observed by Wiedemann [6] in the dehydration of the powdered mineral whewellite ($CaC_2O_4 \cdot H_2O$) at an initial pressure of 10^{-5} torr. As Fig. 10 shows, the effect is very pronounced if powdered material is heated at a rate of 8° per min (part a), much smaller for a single crystal at the same rate, and completely absent for both kinds of samples when heated at 2° per min only (part b). After the rapid apparent weight gain, the expected decrease in weight takes place. So as to be able to describe this effect more precisely, another test was carried out, equal amounts of substance being once housed in a ring beside the empty crucible and once in the crucible on the balance, as illustrated schematically by parts A and B of Fig. 11. The experiment resulted in just the same apparent weight increase for both arrangements (see the dotted TG curve for arrangement A and the solid one for arrangement B in the middle part of the Figure). Simultaneously, a characteristic temporary pressure increase of about one power of ten was equally measured in both parts of the experiment. The test proves that only a fraction smaller than 0.5% of the apparent weight increase can be attributed to a recoil of the molecules leaving the balance pan, but practically the entire effect is due to a re-impact phenomenon. Indeed, it was possible to simulate the same effect on a vacuum thermobalance by introducing measured quantities of gases through a separate inlet into the reaction chamber above the balance pan. As a practical conclusion, in cases where a weight increase occurs upon relatively fast heating of a gas-producing substance under high vacuum, it should always be examined whether such a dynamic phenomenon is present, before other, possibly wrong explanations, e.g. more or less exotic considerations on a chemical basis, are sought for. As experience shows, the dynamic effect decreases with a smaller heating rate; it can also be avoided if much larger pumping cross-sections are used.

On the other hand, the same phenomenon has led Wiedemann and Bayer [29] to an interesting method for a calibration of the temperature in the immediate vicinity of the sample container. To achieve this purpose, the weight effect of defined pressure impulses Δp on the balance pan has been investigated. Figure 12 shows the resulting apparent weight increases caused by impact of gas molecules – the authors worked with CO_2, N_2, O_2, Ar and NH_3 – on the balance pan for constant pressure changes from $1 \cdot 10^{-5}$ torr to $5 \cdot 10^{-5}$ torr (induced by a continuous gas flow) under different isothermal conditions. In agreement with the Maxwell theory, the measured impact forces are proportional to the square root of the absolute temperature and also to the mean velocity of the gas molecules. Thus, it is possible to calculate an unknown temperature in the reaction chamber from the weight effect measured. The method is limited to the vacuum region $< 10^{-3}$ torr, and standard deviations of the temperature of the order of ± 5 K and ± 1 K were obtained at 1225 K and 300 K, respectively. Between 1225 K and

2500 K, the results were considerably less reliable. For a better definition of the limits of this technique, further experimentation is certainly required. Moreover, the same effect was used by Wiedemann [30] to record continuously the mass of gaseous decomposition products simultaneously with the registration of continuous temperature-dependent X-ray diffraction diagrams (TMBA–X-ray method). Another approach to solve the same problem has been described by Gerard [31].



Impact forces M_t weight curve



Pressure curve

Fig. 12. Apparent weight increases caused by impact of gas molecules on the balance pan for constant pressure changes — induced by a continuous gas flow — under different isothermal conditions

In the field of multiple techniques combining TG with numerous other methods, such as DTA, mass-spectrometry, gas-chromatography etc., the number of experimental and apparative parameters which influence the results obtained and therefore need careful control increases markedly. As a systematic discussion of this problem in its full complexity was beyond the framework of the lecture from which this paper is drawn, the authors had rather to restrict themselves to the presentation of a schematical survey of experimental conditions for the case of simultaneous thermogravimetric and gas chromatographic measurements, which may be found in ref. [32]. Moreover, the influence of distinct parameters on the resulting thermoanalytical curves was illustrated by two selected examples. The first one is taken from ref. [28] and compares the TG or DTG curves to the gas-chromatographic (GC) recording for the decomposition of calcium oxalate monohydrate in flowing air. Obviously, a low heating rate must be chosen, as otherwise the GC curve is not determined by a sufficient number of points. Qualitative coincidence is good for the CO and CO_2 peaks above 350°. For water liberated in the region of 150°, however, despite the carefully heated tubing system a time lag of about 15 min had to be accepted due to sorption on the inlet system. In a second, more complex example, gas-chromatography was used for the separation and simultaneous determination of the components water, methanol and carbon dioxide released by thermal decomposition of polygalacturonic acid extracted from apples at different states of ripening. From the carbon dioxide to methanol ratio, the variation of the esterification degree of polygalacturonic acid during the ripening process could be determined (for details see ref. [32]).

Some experimental conditions in differential thermal analysis

In a similar way to the previous discussion for TG, some of the experimental conditions for DTA will next be considered. As a starting point, the theoretical curves for differential temperature and temperature in a DTA experiment with fusion and freezing may be chosen, which are contained in Fig. 13. There, the solid lines hold for the idealized case of a pure non-volatile sample, with extremely small time constant and effective thermal contact, whereas for the broken lines a reproducible thermal contact resistance for both the sample and reference cells is accounted for – an assumption which is very realistic and predicts DTA peak shapes much more resembling those experimentally found. For the freezing process, a supercooling effect is adopted, which, in practice, depends much on the nature of the sample and on the experimental conditions. From the two examples presented, that one at the lower end of the temperature scale – melting and subsequent freezing of metallic mercury, see ref. [33] – fulfils quite ideally the expectation from the case with hindered heat transfer in Fig. 13. In contrast, in the very high temperature region, the curve for melting and solidification of pure corundum in high vacuum shown in Fig. 14 behaves more exceptionally: the

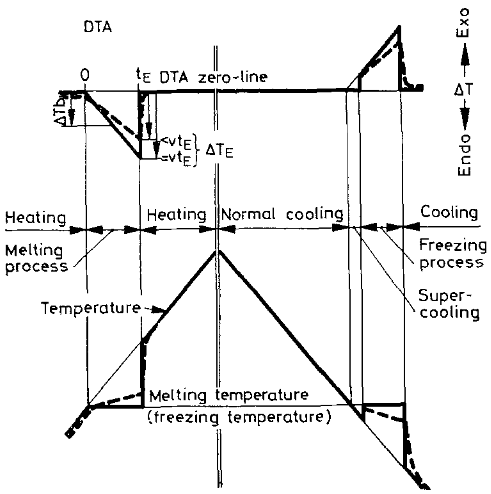


Fig. 13. Theoretical shapes for differential temperature and absolute temperature curves during fusion and freezing; ▬▬ ideal curves for pure non-volatile sample, with extremely small time constant and effective thermal contact; ——— ideal baseline during phase change; – – – curves with reproducible contact resistance for both cells

melting peak near 2100° is followed, upon cooling, by an extremely sharp freezing peak with a drastic supercooling effect amounting to about 170°. Moreover, the TG curve illustrates a loss by evaporation of Al_2O_3 from the melt above 2100° [33].

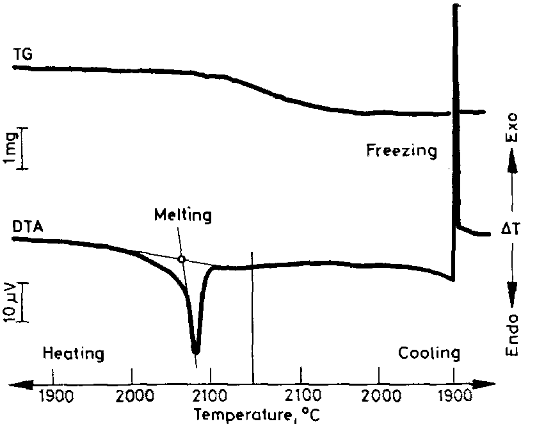


Fig. 14. TG and DTA curves for melting and solidification of pure corundum (sample weight 40.0 mg, heating rate 10°/min, in high vacuum 10^{-5} torr)

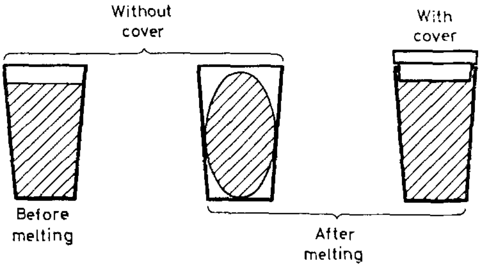


Fig. 15. Behaviour of a lathe-turned metal-pellet sample on fusion in open and in covered crucible

In relation to the heat transfer problem, the shape of the sample is very important. This fact was illustrated, for example, through a detailed investigation into the thermoanalytical characterization of melting and freezing processes and calorimetric calibration of DTA equipment with metal standards by Wiedemann and Van Tets [34]. In particular, some series of DTA experiments with lathe-turned samples of various metals fitting exactly into the cavity of a graphite crucible were undertaken. After the first melting operation, noticeable modifications resulted in the shape of the DTA melting peaks, meaning a marked loss of reproducibility. An explanation is given by the middle part of Fig. 15, the deformation of the metal sample due to surface tension after its first melting, causing an alteration in the degree of contact between sample and crucible wall. To overcome this drawback, a covered crucible was used, specially designed to ensure that the cavity was completely filled by the sample, the weight of the cover being such as to prevent sample deformation and to maintain unvarying contact between sample and crucible wall. The use of a cover has the further advantage of reducing heat exchange between the exposed surface of the sample and the furnace, rendering it less substance-dependent, particularly at high temperatures where heat radiation becomes increasingly important.

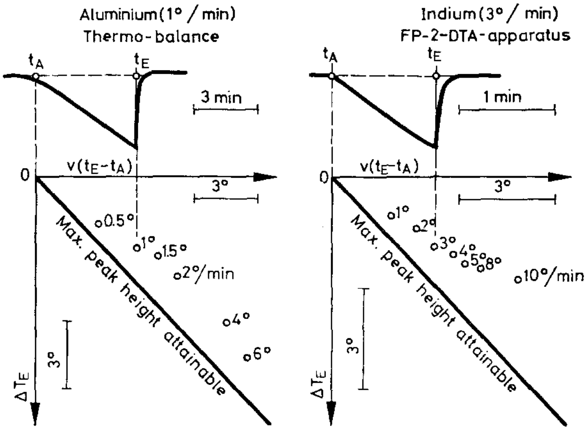


Fig. 16. Actual and theoretically attainable DTA melting peak heights for various rates of heating (left: for aluminium with a cup-type DTA system; right: for indium with a thin-film DTA system)

With such samples of tin, bismuth, aluminium, lead, and silver, cycles of melting and freezing, each conducted at eight different rates of heating and cooling between 0.5 and 10°/min, were recorded. All tests were carried out under repurified, dry argon; the authors state that it is of utmost importance for the gas-flow rate to be kept constant throughout the whole of a run to prevent any heat transfer fluctuation. By graphical evaluation of the results, the theoretical prediction that as regards the melting of a pure sample the maximum temperature deviation ΔT_E in the linearized DTA curves at a relatively small time constant would be approximately proportional to the square root of the heating rate, proved experimentally demonstrable. The same applies to solidification on cooling, provided supercooling can be avoided. Theoretically, when pure samples are used and assuming an isothermal melting process, the melting time is equal to the height of the endothermic peak ΔT_E divided by the heating rate v. This ideal case is only given if at least part of the temperature-measuring element is in good contact with the melting surface. For an illustration, Fig. 16 gives the actual melting peak heights of aluminium and of indium at various rates of heating, compared to the theoretical maximum peak height line derived from the rate of heating of the sample v times the melting time $t_E - t_A$. For aluminium, the data were collected with a cup-type DTA arrangement as described above [34], whereas the data on indium were collected with a thin-film DTA system (see ref. [35]). Because of delays in indication due to thermocouple mass and heat resistance between the sample and the thermocouple, the first-mentioned arrangement is less suited for the precise determination of the temperature of the start of melting. As a consequence of the improved contact between the sample and the temperature sensor and the lower mass of the thermocouple, the beginning of melting is shown without delay using the thin-film DTA system. However, the deviation from the maximum attainable peak height becomes more pronounced at higher rates of heating, due to surface tension effects in the metal, i. e. the formation of a small droplet rather than a thin layer.

During the investigation of very small amounts of cholesterol isolated from gall-stones by the DSC method, it was recently observed in one of the authors' (H. R. O.) laboratories that the characteristic phase transition near 37° appears at somewhat higher temperature in the first heating cycle than on subsequent multiple repetitions after the sample has once been melted [36]. This effect seems at least to some extent related to a change in the heat transfer properties, the sample changing its shape and degree of adherence to the sample pan very markedly, as shown by a detailed scanning electron microscopical investigation. Thus, it can be of rather general importance to take into consideration morphological details when differences in subsequent DTA or DSC runs of small amounts of one and the same sample have to be interpreted.

The effects of the atmosphere and pressure on DTA curves have been demonstrated by numerous investigations. As a particularly illustrative example, the thermal decomposition of calcium oxalate monohydrate in air at various pressures between 720 and 10^{-5} torr is cited [27]. The most influenced group of DTA peaks lies between 400 and 500° and corresponds to the reaction leading from anhydrous calcium oxalate to the carbonate. The liberated carbon monoxide is completely oxidized between 720 and 100 torr (exothermic character), partially oxidized between 1 and 10^{-2} torr, and no longer oxidized below 10^{-2} torr (endothermic character). Significant differences in the DTA curves of magnesium sulphate heptahydrate under reduced and normal pressure have also been observed by Rassonskaja [37].

By DTA and simultaneous TG measurements, another determination of vapor pressure becomes practicable, as described by Pfefferkorn and Wiedemann [38], but – in contrast to the thermogravimetric Knudsen method mentioned earlier – in the range between 1 and 760 torr. The principle consists in housing the sample and reference substance in specially designed aluminium crucibles, with a hole in the cover closed by a small steel or sapphire ball so as to form a valve which opens when the inside pressure reaches a value higher than the outside pressure plus the weight of the ball. Such ball-valve crucibles have been used previously by Forkel [39] for thermal analytical investigations of reactions under "self-generated" atmospheres. The tests described in ref. [38] were effected under different isobaric conditions, and the assumption was made that the measured pressure was identical to that of the vaporized substance, i.e. that phase equilibrium had been attained. In practice, a sensitivity of 200 μV on the chart and a heating rate of 10°/min were chosen. The outside pressure was measured with a Thommen barometer (1 scale division = 1 torr). Boiling temperature was measured using the extrapolated endothermic peak onset temperature as the boiling point. For thermal calibration the three metals tin, indium and gallium were used. In Fig. 17, the principle of the method is illustrated by the simultaneous

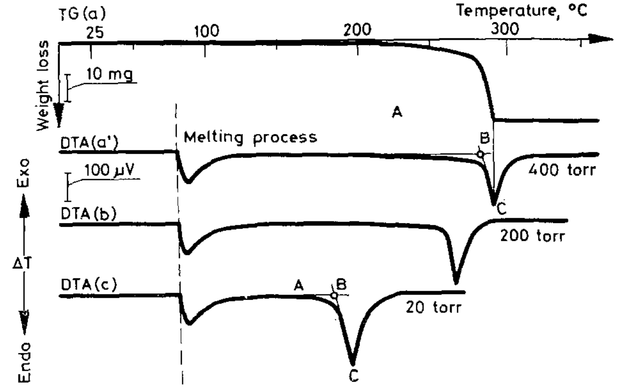


Fig. 17. Simultaneous TG—DTA curves of o-acetophenetidide (a and a') measured in a ball-valve crucible at various external pressures (sample weight 25 mg, heating rate 4°/min). A) start of vaporization; B) boiling point; C) end of vaporization

TG—DTA curves of o-acetophenetidide registered at various pressures. The weight of a sapphire ball used in practice was, for example, equal to 3 torr. Compared to literature values, the average error in the boiling temperature at various external pressures as determined by this technique for several organic substances is less than 2%. In addition, the enthalpy of vaporization was calculated. In an extended review, Newkirk [40] has discussed different types of crucibles for "self-generated" atmospheres and particularly for their application to vapor pressure determination under different pressures.

As the DTA melting peak of a volatile substance can in many cases be considerably affected by the increasing influence of evaporation — an example is benzoic acid — the use of such ball-valve crucibles can also be helpful in the determination of correct melting peak areas.

Conclusion

A principal aim of this article was to illustrate the introductory statement that thermal analysis is becoming progressively quantitative. However, it was also intended to show, although by an arbitrary and incomplete selection of examples, how much thermal analytical curves, and hence the quality of the results derived therefrom, are dependent on the experimental conditions applied.

A valuable support for quantitative thermal analysis is provided by using approved standard reference materials for various purposes, in order to achieve a better comparison of results obtained in different laboratories on a world-wide scale. Three sets comprising ten certified temperature standard materials are available for DTA, covering the range from 125° to 940°; these have been selected and submitted to a broad test program by the International Confederation for Thermal Analysis (ICTA) through its Committee on Standardization, in liaison with the U.S. National Bureau of Standards [41]. Similarly, there exist ICTA-NBS certified reference materials for the temperature calibration of DTA from 180 K to 330 K [42] and for the standardization of glass transition temperatures in polymers [43]. Further standard materials destined for temperature calibration in TG and high-temperature DTA, as well as for measurements of enthalpy changes and purity determinations, are still under investigation at present. Moreover, reference may be made to the available NBS standards for gold vapor pressure [44] and for the specific heat function of synthetic sapphire, α-Al_2O_3, between 273.15 and 2250° [45].

Considerable improvement in recognition and subsequent avoidance of various influences on thermal analytical curves can be expected from automatic data collection and evaluation procedures. These techniques result in faster and better quantitative findings about the quality of measurements, e.g. through the availability of standard deviations. Further, the linearization of temperature programs diminishes errors in the interpretation of curves, and effects such as the buoyancy influence can be corrected for in the data evaluation computer programs.

Those effects which can be minimized by a better knowledge of the particular character and the previous history of a given sample should be taken into account by the analyst, as well as the consequent observance of optimated conditions of measurement. On the other hand, the amelioration of control over factors such as the stability of the balance regardless of the varying atmosphere, DTA baseline drift, etc., lie on the side of the further technical progress to be achieved by the producers of thermal analytical equipment.

There is indeed a continuous strong need for detailed and careful basic research work in order to achieve a better control over all sorts of experimental factors. But valuable support is also necessary and possible from the mere "consumers" of thermal analytical methods, mainly by applying sufficient criticism to their own results and via the will to improve them as much as possible by taking better care of their experimental conditions.

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Résumé — On passe en revue les conditions d'expériences qui influencent les résultats de l'analyse thermique et on les classe en trois groupes: les propriétés de l'échantillon, les paramètres d'expérience et les paramètres propres aux appareils. On discute, à l'aide d'exemples, quelques conditions d'expérience, en considérant surtout la TG et l'ATD. On examine en particulier la grandeur des particules, l'atmosphère en tant que partie du système réagissant et en tant que paramètre d'expérience, le problème de la force ascensionnelle, le phénomène de choc dynamique répété des molécules, le transfert de chaleur et les problèmes de retard à la fusion lors du refroidissement ainsi que l'ATD sous diverses conditions isobares. Lors de l'analyse thermique quantitative, les conditions d'expériences doivent être minutieusement contrôlées. L'emploi de substances étalons de référence ainsi que l'acquisition et le traitement automatiques des données peuvent contribuer à parvenir à de meilleurs résultats.

Zusammenfassung — Die die thermoanalytischen Ergebnisse beeinflussenden Versuchsbedingungen wurden zusammengefaßt und in drei Gruppen unterteilt: Eigenschaften der Probe, Versuchsparameter, Parameter des Geräts. An Hand ausgewählter Beispiele werden einige Versuchsbedingungen, hauptsächlich betreffs TG und DTA, erörtert. Eine besondere Aufmerksamkeit wird der Partikelgröße, der Atmosphäre als Teil des Reaktionssystems und als Versuchsparameter, dem Problem der Auftriebskraft, dem dynamischen Wieder-Einschlagphänomen der Moleküle, der Wärmeübertragung und den Problemen der Unterkühlung beim Schmelzen und der DTA bei verschiedenen isobaren Bedingungen gewidmet. Bei der quantitativen Thermoanalyse benötigen die Versuchsbedingungen ein sorgfältiges Regeln. Standard Referenzsubstanzen sowie Techniken der automatischen Datensammlung und -verarbeitung können zum Erhalten besserer thermoanalytischer Ergebnisse verhelfen.

Резюме — Экспериментальные условия, затрагивающие термоаналитические результаты, обобщены и подразделены на три группы: свойства вещества, экспериментальные и аппаратурные параметры. На примере выбранных образцов обсуждены некоторые экспериментальные результаты, главным образом для ТГ и ДТА. Особое внимание уделено размеру частиц, атмосфере как части реакционной системы и как экспериментальному параметру, проблеме плавучести, явлению динамического соударения молекул, проблемам переноса тепла и сверхохлаждения при плавлении и ДТА при различных изобарных условиях. В количественном термическом анализе экспериментальные условия требуют тщательного контроля. Стандартные материалы сравнения наряду с техникой автоматического сбора данных и обработки, помогают достичь лучших термоаналитических результатов.