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# THE TG BASE LINE

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Situations were investigated when changes in the TG curve are observed which are not induced by changes of the sample mass. These changes are explained as changes of displacement forces acting on the sample during the experiment. The conception of the TG base line is proposed.

Changes in the position of the TG curve, are often observed which are not induced by changes of the sample mass. Even when both the composition of the gas atmosphere inside the furnace and the heating rate are invariable, the TG curve for a thermally stable sample moves in the direction of mass increase if the furnace is heated up. In the initial period of heating these changes are rapid, but later they are slow and smaller. Changes of the heating rate and of the composition of the gas atmosphere also cause corresponding changes in the TG curve position. It is evident that neglect of these changes will cause inevitable errors in the interpretation of TG data.

Under well-defined experimental conditions (the thermobalance, the geometry of the sample holder and pans, the nature of the programs of temperature and gas composition changes), the shape of the TG curve reproducible. Let us call the TG curve for the thermally stable sample ($m$ = const), recorded under conditions corresponding precisely with the experimental ones, the TG base line, similarly as for the concept of the DTA base line [1, 2].

The inspection of situations where the sample mass is constant, whereas the TG curve is not horizontal during the experiment, reveals that this is caused by changes in the value of the displacement force acting on the sample system (the sample holder, the pans and the sample), mostly because of changes in the density of the gas medium inside the furnace.

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## Physical principles and discussion

A weight force and a displacement force act on the sample system. The resultant of these forces acts on the balance arm and is recorded as the TG curve. It holds that

$$m_1 = m - V * d$$

where $m_1$ is the sample system mass according to the TG curve, $m$ is the real sample system mass, $V$ is the volume of the sample system, $d$ is the mass density of the gas medium inside the furnace. This means that all changes of the real sample mass, of the sample volume and of the density of the gas medium may cause corresponding changes in $m_1$, i.e. changes in the TG curve shape.

In the case of a thermally stable sample (or an empty pan), we have $m =$ const and $V =$ const. Then, it is easy to see that $m = f(d)$, i.e. in this case the position of the TG curve is dependent only on the density of the gas medium. As this is different for the various gases, and for each one is dependent on temperature, changes of the temperature and the gas composition cause resultant changes in the TG curve, giving (for $m =$ const) the TG base line for the experiment.

It is self-evident that the TG curve shifts caused by changes of temperature, gas composition and sample volume will overlap. Under real experimental conditions, the TG base line may therefore assume a complex shape, as demonstrated below.

## Experimental

Experiments were carried out with the Mettler TA 2 thermal analyzer, which has the control thermocouple inside the furnace. The macro-type of DTA sample holder and platinum pans (0.9 $cm^3$ capacity) were used. The apparatus was modified to allow easy, rapid and reproducible changes of the gas composition inside the furnace. The essence of the modification is the additional gas inlet. Thus, gases may flow in two ways inside the furnace: one gas stream through the balance (gas inlet 1), and the other one directly inside the furnace (gas inlet 2). These two gas streams are mixed inside the furnace. In our laboratory pure argon is fed through gas inlet 1 (0.5 $cm^3/s$) and argon or air or hydrogen (or another active gas) through gas inlet 2 (in a suitable amount). The composition of the gas medium inside the furnace can thus be easily controlled.

Example 1. Thermogravimetric determination of carbon black content in polyethylene

Sample: Low-density polyethylene mixed under laboratory conditions with 2.00 per cent carbon black.

Experimental conditions: Sample 20.00 mg; gas atmosphere argon; heating rate 10 deg/min from ambient temperature up to 600°. This temperature is held constant during the change from argon to air under isothermal conditions. TG base line: obtained under the above conditions with the empty pan.

T, TG and DTA curves and the TG base line obtained are shown in Fig. 1. The contents of carbon black were determined as 1.5 per cent without, and 2.0 per cent with consideration of the TG base line. It is clear that a correct result is obtained only if the real TG base line is considered. Neglect of the TG base line gives an error of 25 relative per cent, which may be still greater for a smaller sample mass and/or for a lower carbon black content in the sample.

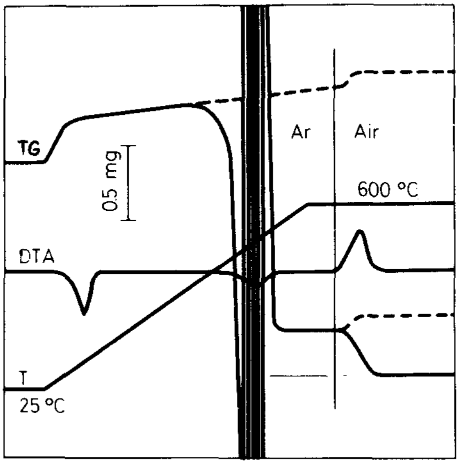

Fig. 1 The determination of the carbon black content in polyethylene. Broken line: TG base line determined by an independent experiment

Example 2. Analysis of forces in qualitative interpretation of the TG curve

During heating of the fused sodium formate – sodium hydroxide system, reaction may occur [3]:

$$HCCONa + NaOH \rightarrow Na_2CO_3 + H_2$$

The TG curve then has a surprising shape (Fig. 2). Inspection and analysis of the physical behaviour of the reacting mixture and the reaction products (solid and gas) reveal the reason for the complicated shape of the TG curve. It appears that the reacting mixture undergoes foaming while giving off hydrogen. This causes a temporary, but considerable increase of the sample volume, up to the total capacity of the pan; the displacement force at this time has the maximum permissible value (Fig. 2, point b). At the moment when the bubble bursts, the sample volume is reduced to nearly the previous volume (Fig. 2, point c); the displacement force is reduced too.

Thus, the correct shape of the TG curve, corresponding to the reaction run, is near the upper of the recorded curve, and this must be used in the quantitative (e.g. kinetic) interpretation of these TG data.

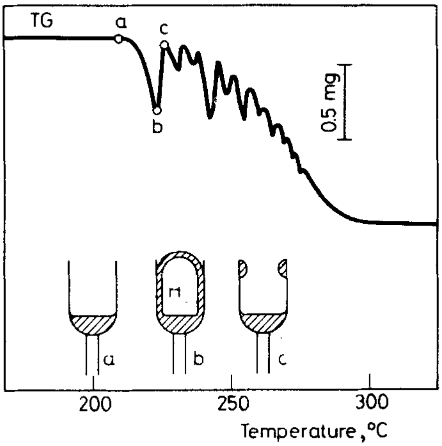

Fig. 2 The TG curve of sodium formate – sodium hydroxide system

## Comments

The considerations and examples presented show the possibility of the influence of the displacement phenomena on the results of TG experiments. The changes in the TG curve (base line) are not large in the absolute scale but they are perceptible. They are reduced more and more if small samples and micro-types of sample holders are used. However, at times they can not be neglected. If they are to be taken into consideration, the TG base line under the conditions corresponding to the definite experimental ones should be recorded as the curve for the thermally stable sample.

## References

1 D. Schultze, Differentialthermoanalyse (in Polish), PWN, Warszawa, 1974.

2 W. Balcerowiak and Cz. Latocha, J. Thermal Anal., 17 (1979) 305.

3 W. Balcerowiak and J. Wasilewski, Proceedings of the 3rd Seminar of S. Bretsznajder, Płock, 1983.

**Zusammenfassung** — Es werden Situationen untersucht, bei denen Änderungen der TG-Kurve beobachtet werden, die nicht auf Änderungen der Probenmasse zurückgeführt werden können. Diese Änderungen werden als Änderungen der Auftriebskräfte an der Probe während des Versuchs gedeutet. Die Konzeption einer TG-Basislinie wird vorgeschlagen.

РЕЗЮМЕ — Исследованы положения, когда наблюданмые изменения кривых ТГ вызваны не отклонениями в весе образца. Такие изменения объяснены как изменение сил смещения, действующих на образец во время эксперимента. Предложено понятие ТГ базисной линии.