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Instrument dependence and influence of heating rate, mass, ΔH, purge gas and flow rate on the difference between the experimental and programmed temperature of the instrument

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Abstract

It has been observed that for endothermic decomposition processes a thermal analysis unit may fail to follow the programmed temperature. A more thorough study shows that the magnitude of the failure of a thermal analysis unit, i.e. the difference between the experimental and programmed temperature, is dependent on the type of the instrument and is also influenced by the heating rate, the mass of the sample, the enthalpy change (ΔH) of the process, the purge gas and the flow rate. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Experimental conditions; Instrumental errors

1. Introduction

It is well known that experimental conditions may influence considerably thermal measurements [1–3] which may give problems in comparing results from different experiments. Recently several authors mentioned this problem without further investigation of the reasons [4–11]. In our opinion this problem originates from the fact that the instrument cannot maintain its programmed temperature (heating rate) when endothermic (or eventually exothermic) processes occur. This effect is well known as one can make use of it at the temperature calibration of a TG-analyser [12]. In this study the magnitude of the influence of several experimental conditions on the difference between the experimental and the programmed heating rate, i.e. the type of instrument, the heating rate, the mass of the sample, the ΔH of the process, the purge gas and the flow rate, is studied for some endothermic processes. These experimental parameters considerably influence the experimental temperature and consequently must be kept constant to compare results from different experiments.

2. Experimental

All chemicals and metals were bought from Aldrich with a purity higher than 99%. $Mn(urea)_2Cl_2$ has been synthesized by refluxing stoichiometric amounts of urea and $MnCl_2$ in a small volume of anhydrous ethanol until a pale pink solid precipitates. This solid was filtered, washed with ether and dried under vacuo at room temperature [13].

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The thermal analysis experiments were performed on the TGA-2950 and the SDT-2960 Modules of TA-Instruments. Experimental conditions differ for the different experiments in this paper and will be described in more detail at the beginning of each section. Each experiment has been performed twice to check for its reproducibility.

3. Results and discussion

3.1. Instrument dependence and influence of the heating rate

By studying the thermal decomposition of manganese–urea (U) complexes at linear heating rate, it is observed (see Fig. 1) that, at the endothermic decomposition step of MnU_2Cl_2 to MnU_1Cl_2 (ΔH=110 kJ/mol) the instrument could not follow its programmed temperature.

Fig. 2 shows the plot of the first derivative of the temperature with respect to time, or the time dependence of the experimental heating rate. It is clearly seen that the instrument cannot follow its programmed temperature at the beginning of the process. In order to attain the programmed temperature again, the oven needs to warm up the sample at a higher heating rate than the programmed. This results in a delay followed by an overshoot of the experimental heating rate.

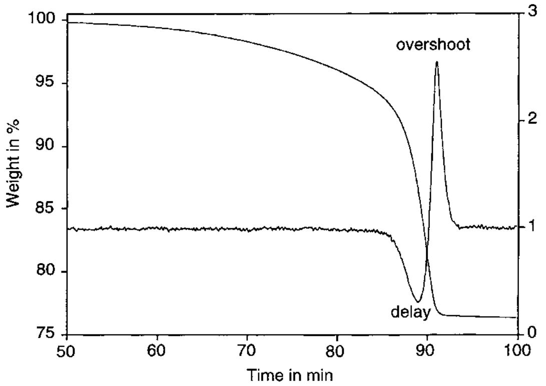

Fig. 2. Experimental heating rate at the endothermic decomposition step.

Fig. 3 shows the plot of the maximum delay and the maximum overshoot of the experimental heating rate against the programmed heating rate. This experiment was performed on two different instruments, the TGA-2950 and the SDT-2960 of TA-Instruments. The sample mass has been kept constant at approximately 10 mg and dry N_2 was taken as the purge gas at a flow rate of 50 ml/min. This figure shows that the difference between the experimental and the programmed temperature of the instrument increases with increasing heating rate.

It was also observed that this temperature difference is instrument dependent. This fact is probably caused by the different constructions of the instruments: in the TGA-2950 there is a distance of approximately 0.5 cm between the thermocouple and the sample in contrast with the SDT-2960 where the thermocouple is right

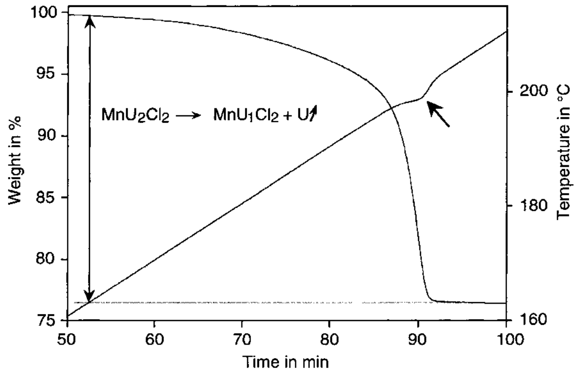

Fig. 1. Influence of the endothermic decomposition on the experimental temperature at a programmed heating rate of 1°C/min.

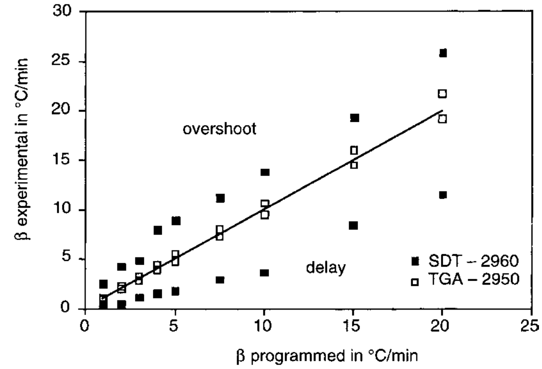

Fig. 3. Instrument dependence and influence of heating rate (β) on the difference between the experimental and programmed temperature.

under the sample pan. Because of the temperature gradient in the direct neighbourhood of the sample (temperature difference between the oven and the sample during the endothermic decomposition process) this effect is more clear in the SDT-2960-module with its shorter distance between the sample and the thermocouple.

As the effect is more visible on the SDT-2960-module this instrument was used for all the other measurements performed in this study. The results of these measurements are discussed in Sections 3.2–3.4.

3.2. *Influence of the mass of the sample*

Fig. 4 shows the temperature against time plot of different sample masses at a linear heating rate of 10°C/min for the endothermic decomposition process of MnU_2Cl_2 to MnU_1Cl_2. Again dry N_2 was taken as the purge gas at a flow rate of 50 ml/min. The deviation of the experimental from the programmed temperature increases with increasing sample mass.

Fig. 5 shows that the total delay surface and the total overshoot surface of the experimental heating rate are, within experimental errors, equal as the instrument reaches its programmed temperature again. These surfaces describe the integration of respectively the delay and the overshoot during the whole process. It is better to consider these surfaces than the maximum delay or the maximum overshoot because they describe the effect of the full process. The maxima only describe the effect at one point of the process and are dependent on the shape of the temperature versus time plot: sharp peaks give larger maximum values than broad peaks although the total effect (surface) may be the same or even reversed in magnitude. In the previous section these surfaces were not considered because of the very small values and consequently very big calculational errors of the surfaces measured by the TGA-2950 module.

Fig. 6 shows the plot of the total delay surface and the total overshoot surface of the heating rate as a function of the mass of the sample. It can be clearly seen that these surfaces increase with increasing sample mass. At higher sample masses more molecules take part in the endothermic decomposition process and more heat is taken from the direct environment of the sample.

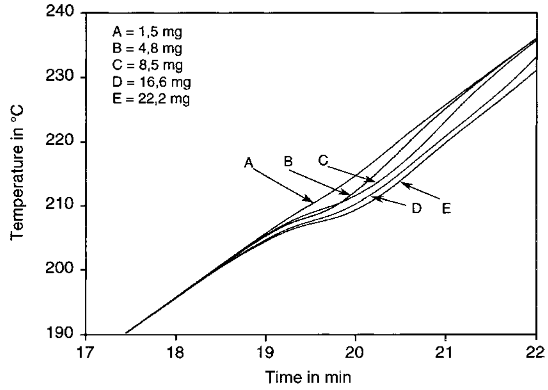

Fig. 4. Influence of sample mass on the experimental temperature.

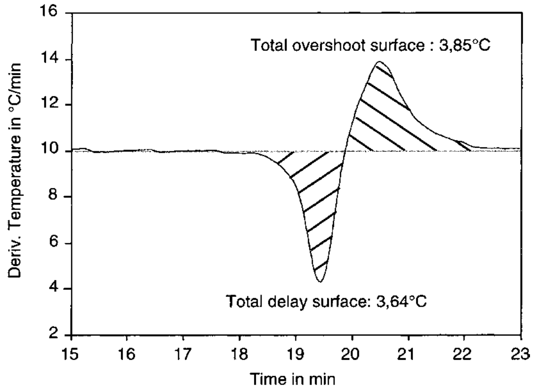

Fig. 5. Experimental heating rate in the endothermic decomposition region with a sample mass of 4.8 mg at a programmed heating rate of 10°C/min.

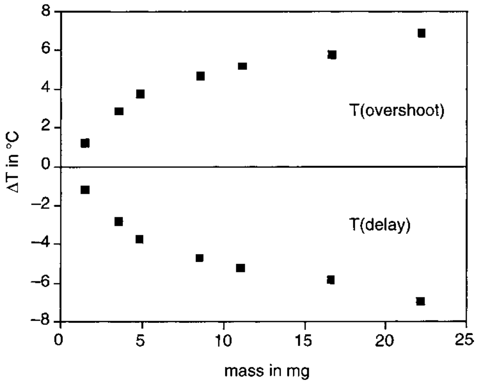

Fig. 6. Sample mass dependence of the total delay and overshoot surface of the experimental heating rate.

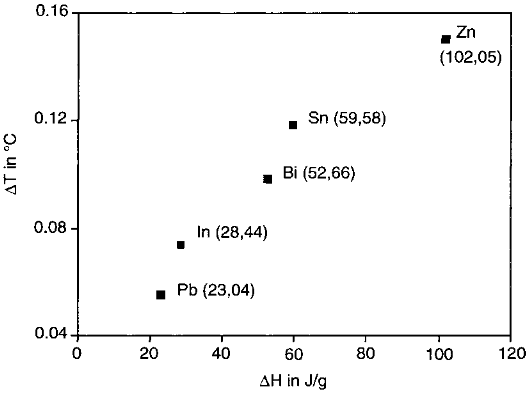

Fig. 7. ΔH-dependence of the total delay surface of the experimental heating rate, the ΔH-values are given between parenthesis in J/g.

3.3. Influence of the ΔH

To study the influence of ΔH on the difference between the experimental and the programmed temperature, the melt of several metals, namely In, Sn, Bi, Pb and Zn, was studied. A sample mass of ca. 20 mg was studied for each sample at a heating rate of 10°C/min. Again dry N_2 was taken as the purge gas at a flow rate of 50 ml/min. The best results were obtained in closed containers because the heat is spread out better over the sample and consequently the melting peaks became sharper and undivided compared to the experiments in open containers.

Fig. 7 shows the plot of the total delay surface of the heating rate against the ΔH of the melting process studied. We clearly see that this surface increases at increasing ΔH-value. At higher ΔH-values (expressed in J/g) more heat is taken from the direct environment of the sample for the same mass of product. Physically there is no difference with the study of the different sample masses described in the previous section in which the different amount of energy is caused by the different amount of product taking part in the total process and not by the ΔH-value of the process itself.

3.4. Influence of the purge gas and the flow rate

The endothermic decomposition of 10 mg of MnU_2Cl_2 to MnU_1Cl_2 at a heating rate of 10°C/min was studied in different dry purge gasses (N_2, Ne and He) and at different flow rates (15, 25, 50, 75, 100 and 125 ml/min). N_2, Ne and He were chosen because of their different heat conductivity: 66, 121 and 376 (cal/s cm^2 (°C/cm) 10^{-6}) respectively at a temperature of 50°C.

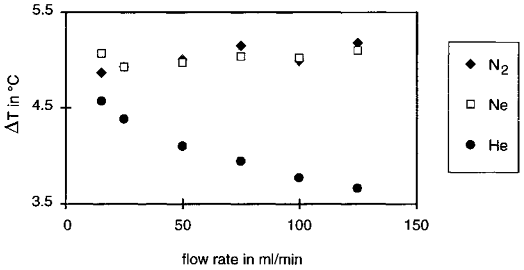

Fig. 8. Flow gas and flow rate dependence of the total delay surface of the experimental heating rate.

Fig. 8 shows the influence of the different purge gasses and the different flow rates on the total delay surface of the experimental heating rate.

This total delay surface does not depend on the flow rate in the case of N_2 and Ne. The influence of N_2 and Ne on the total delay surface is also comparable (ca. 5°C). When we use He we clearly see that the temperature difference is smaller compared with N_2 and Ne and that it decreases at increasing flow rates. Because of the higher heat conductivity of He heat diffuses better from the oven to the sample and the temperature difference is much more compensated. This heat diffusion process also proceeds better at higher flow rates. The heat conductivities of N_2 and Ne are not sufficient to influence this temperature difference.

4. Conclusions

By studying processes in which the heating rate is important, i.e. the study of the activation energy by thermogravimetry at constant heating rate, one must take care not to compare results measured with different instruments. It is also better, if possible, to keep the heating rate, the initial mass of the sample, the ΔH-value of the process studied, the purge gas and the flow rate, constant when results from different experiments are compared, as it was shown in this paper that these experimental conditions may significantly influence the magnitude of the failure of a thermal analysis unit, and consequently the magnitude of the experimental errors of the experiments. Closed containers, if allowed by the experiments, are also preferred. Of course it would be difficult to study the decomposition processes in a closed container when gas is evolved. In this case it can be useful to make a small hole in the cap of the container so that the heat is still spread out better over the sample than with open containers, but so that the gas is allowed to evolve the sample.

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