

FACTORS AFFECTING THE EXPERIMENTALLY RESOLVED SHAPES OF TG CURVES

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From a theoretical consideration concerning the factors affecting the experimentally resolved shapes of thermogravimetric curves, the possible way to increase the accuracy of the thermogravimetric measurements were discussed.

Keywords: kinetics, shapes of TG curves

Introduction

Although the present thermogravimetric (TG) apparatuses have achieved a very sophisticated state [1-7], the information obtained from the experimentally resolved shapes of TG curves is still at the level of qualitative characterization of the reaction temperature and rate [8]. On the other hand, as is the case of the use of TG curves as a source of kinetic data, the accuracy of the TG measurements have always been desired [9]. The accuracy of TG data is not only limited by the sensitivity of the balance, but by the magnitude of spurious effects due to the conditions of the experiment. Further sophistication would be enabled by solving the problems connected within unified concept of the fluid density gradients convenient to describe melts behaviour during single crystal growth [10], as adopted for discussion in the present paper.

Problems

Gradients in the atmospheric density and temperature

In the closed system shown in Fig. 1, gradients in both the atmospheric density, ρ , and temperature, T , should be arose. These gradients are also affected by

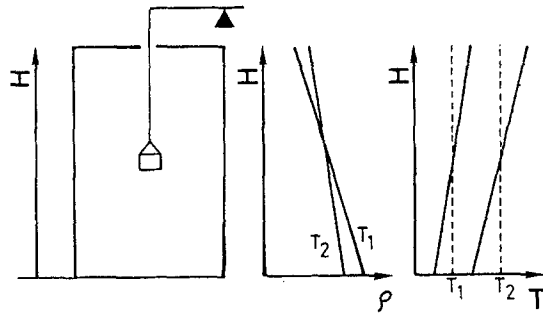


Fig. 1 Density, ρ , and temperature, T , gradients within the closed TG system

the temperature of the system. In the case of $\rho \ll$, e.g., in vacuum, both the gradients and their temperature dependence can be ignored. On the other hand, the correct measurement of sample mass is disturbed by these factors and shift of TG base line would be observed, when the ρ is large enough. Typical example is the case of measurements of crystal growth from fluid [11].

Atmospheric flow caused by heating

When the closed system were heated from outside, a kind of heat flux, \dot{q} is arose within the system (Fig. 2(a)). In the gaseous atmosphere, the heat flow is governed by the conduction or convection. When ρ is large enough, this is accompanied by the flow of atmosphere, \dot{f} , as shown in Fig. 2(b).

In addition, the gradients in T and ρ would be also observed in the vertical direction (Fig. 3). These gradients introduce the mixing flow shown in Fig. 3. It

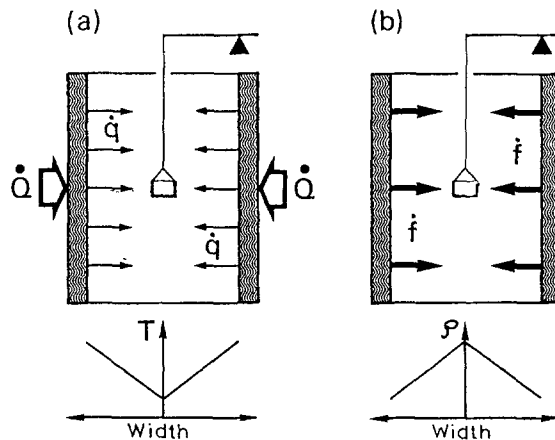


Fig. 2 (a) The heat flow, \dot{q} caused by the furnace heating, \dot{Q} , and (b) consequent flow of atmosphere \dot{f}

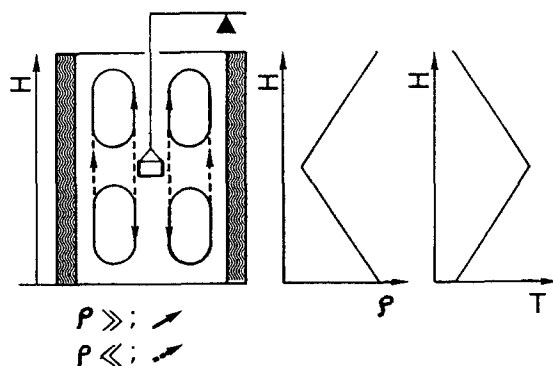


Fig. 3 Density, ρ , and temperature, T , gradients caused by dynamic heating and consequent mixing flow of atmosphere

is worth noting that the change of melt stirring and/or crucible rotation can create temperature changes in order of degrees which is particularly acknowledged during the growth of single crystals from melts [11]. These kind of circulation pattern may also offer a good explanation for the common fact that the apparent increase in weight only partly follows the temperature. Although the apparent weight changes do generally imitate the temperature pattern, frequently the magnitude of those changes is not proportional to temperature, as shown in Fig. 4(a). The noise in the apparent weight is actually a cyclic pattern of oscillations of weight, following the slight oscillation of the temperature. Figure 4(b) shows the change in the measured weight and buoyancy with temperature. Difference between these two curves represent the forces caused by circulations of the gas in the temperature field. These forces are added to the static-buoyancy component.

Inert gas flow system

Both the gradients in T and ρ and consequent flow of atmosphere can be avoided by opening the system with introducing the inert gas flow (Fig. 5(a)). In this case, however, the partial pressure, Δp , results from the gas flow. The mass measurements are affected by Δp . The Δp can be reduced by the use of non-linear reaction tube which introduces the 'labyrinthine paths' of gaseous flow (Fig. 5(b)). The main intention of the 'labyrinth path' is to allow the forced gas flow, while reducing or eliminating any gradient-related circulation. A practical conclusion is that those TG instruments which allow baffling the volumes above and below the sample holder, permit the oscillations to be reduced or stopped, while allowing the desired and laminar flow of the reaction environment; thereby yielding more accurate results. Counter flow of the inert gas is also effective to cancel the Δp by the Δp compensation (Fig. 5(c)).

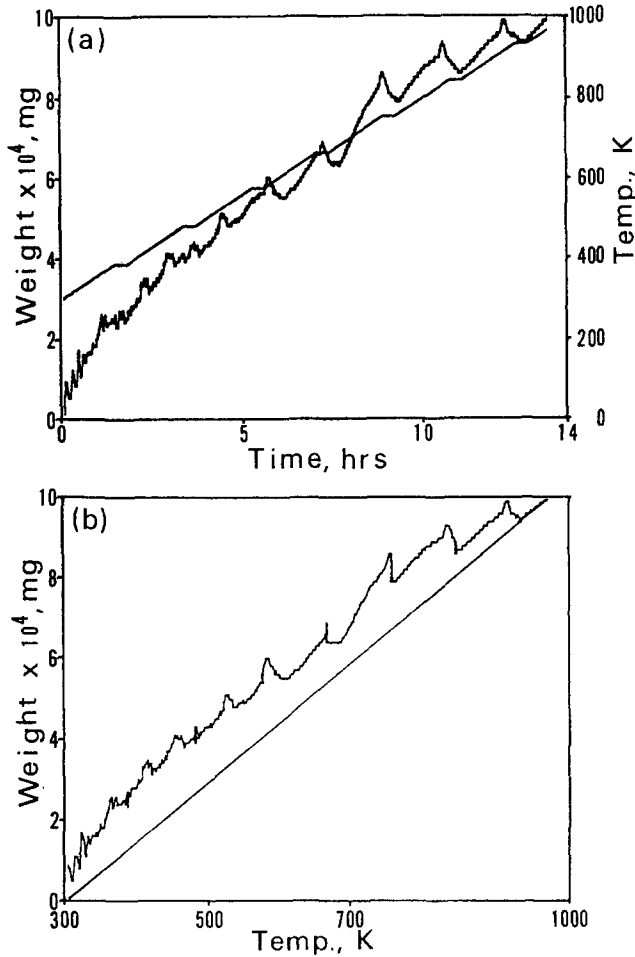


Fig. 4 (a) Change of the apparent weight with stepwise heating (sample size $20 \times 20 \times 20$ mm)
 (b) Disproportion of the apparent weight to temperature as in (a), straight line represents the static buoyancy calculated

Surface reflectance of the sample cell

Temperature distribution within the TG system should be affected by the reflectance of the sample cell surface. The reflectance can be classified into three type;

- (i) reflective (Pt-radiation shield),
- (ii) absorbent (carbon 'black-body') and
- (iii) transmittant (quartz).

Figure 5 shows the temperature distribution for (i) and (ii). In the case of (iii), the distribution is determined by the nature of the sample. The effect of reflectance is significant for the measurements under vacuum.

As can be seen from (Fig. 6(a)), the temperature difference between the sample and temperature sensor is also affected by the surface reflectance of sample cell. This can be reduced by covering the sensor with the cell same with the sample cell, as shown in Fig. 6(b).

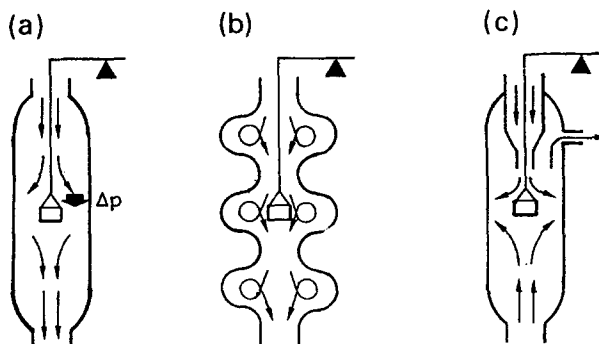


Fig. 5 (a) Inert gas flow and the partial pressure, Δp , caused by the flow, (b) non-linear reaction tube which introduce the labyrinthine paths of gaseous flow and (c) Δp compensation in the counter flow system

Further improvements in temperature measurements can be achieved by calibration [12], where measurement of the temperature difference between the sample and the reference crucible is made prior to the entire experimentation. Practically, it is accomplished by suspending the upper crucible on two thermocouple wires and measuring the temperature difference as a function of increasing temperature for the given heating rate. Additional accuracy can be attained by checking the absolute temperatures of at least three reference points; for example, optically by placing a few crystals of weight stable substances on the upper crucible and observing their melting points, e.g., dinitrobenzene (90°C), KNO_3 (333°C), Ag_2SO_4 (652°C).

Sample setting

In the nonisothermal measurements, the sample is set up in the TG system before measurements and heated at a constant heating rate, Φ . On the other hand, in the isothermal analysis, the sample is heated at a Φ to a desired temperature and then maintained at that temperature. This procedure is not always successful, because the reaction sometimes starts before the sample reaches at a desired temperature. The accuracy of the isothermal TG curves are largely de-

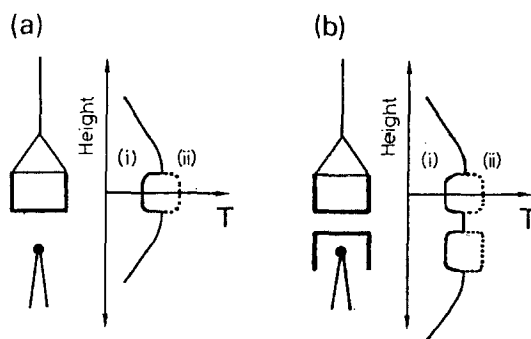


Fig. 6 (a) Temperature distribution caused by the difference in the surface reflectance of the sample cell; (i) reflectant and (ii) absorbent, and (b) covering of the temperature sensor

creased by such a temperature background. This is avoided somewhat using the IR heating ensuring the higher Φ [13, 14]. Another possibility is the 'drop-in method [15]' for setting the sample, in which the sample is inserted to the furnace after the furnace reached to the desired temperature. Figure 6 shows the procedure schematically. The metal block suspended at the end of balance is first heated to a desired temperature (Fig. 7(a)). Subsequently, the sample cell is inserted along the suspending wire to fit geometrically on the block-conus assuring thus good heat conduction from the heat reservoir (Fig. 7(b)); of course, by temporally clumping the balance during setting.

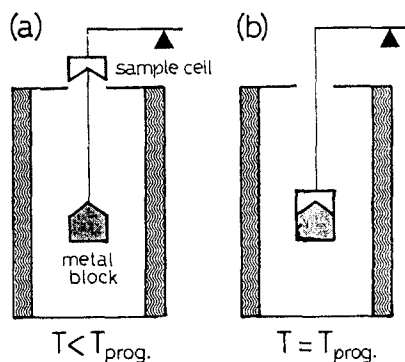


Fig. 7 Drop-in method for setting the sample (adopted after [15])

Self-generated conditions

Because TG can only be applied for the reaction accompanied by mass-change, TG curve, i.e., the course of reaction, is affected by the atmospheric conditions generated by the reaction itself. During the thermal decomposition of solids, the change and gradient in the partial pressure of the evolved gas, Δp ,

should be observed within the sample matrix. Figure 8(a) shows the change in Δp during the reaction. Usually, the change in Δp is not taken into account on interpreting the TG curves. This problem can be reduced somewhat by decreasing the sample size (mass) and applying the temperature condition which leads the moderate reaction rate. In this sense, the constant rate thermal analysis (CRTA) [16] has a merit, because the self-generated condition remains constant during reaction, at least, compared with the traditional isothermal and nonisothermal measurements. One of the author of this paper has the opposite opinion on the small-sample recommendation [17, 18], because small samples make even poorer correlation with large-scale processes and also experience shows that even very small samples (less than 1 mg) are far from being small enough to be free of diffusion inhibition. That applies also to the issue of CRTA: although CRTA indisputably produces faster TG runs, by reducing the inter transition periods, it results misleading in the area of determination of the temperature limits of thermal stability of substances [19].

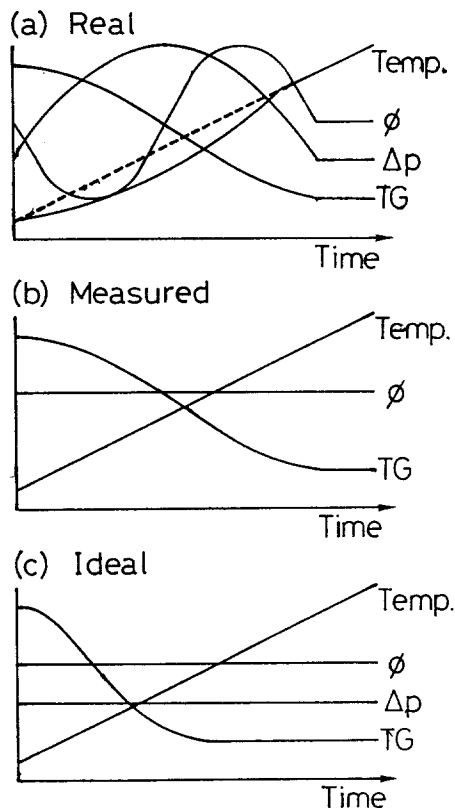


Fig. 8 Changes in the partial pressure of evolved gas, Δp , and heating rate, Φ , during the course of endothermic reaction

The distortion of the programmed temperature change by the enthalpy change during the reaction is another serious problem caused by reaction itself [20]. This is well-known as the self-cooling and self-heating effects. In contrast to the DTA measurements in which the deviation is the measured quantity [21], in TG the deviation is not always detectable [22] (Fig. 8(b)), because of the bad contact between the sample and temperature sensor.

In order to increase the accuracy of TG curves, the comparison of the TG curves obtained at an ideal condition (Fig. 8(c)), i.e., constant Δp and Φ during the reaction, and in conventional way is necessary. A kind of standard reaction should be established for this purpose [23]. Here, it is termed 'kinetic standard'. The kinetic standard does not have any additional calibration for its object, but does have a role to estimate the accuracy of the TG curves.

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Zusammenfassung — Unter theoretischen Aspekten bezüglich derjenigen Faktoren, die die experimentelle Auflösung thermogravimetrischer Kurven beeinflussen, wird ein möglicher Weg zur Steigerung der Genauigkeit thermogravimetrischer Untersuchungen diskutiert.