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SIMPLE ESTIMATION OF THE TEMPERATURE ERROR IN THERMOGRAVIMETRIC EXPERIMENTS

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ABSTRACT

Two simple expressions are presented for the calculation of the maximum temperature difference between the centre and the outer boundary of a sample during a temperature-programmed TG experiment. The results obtained using these formulae are compared with those obtained with a classical heat transfer/chemical reaction model of a devolatilization reaction. The formulae give an excellent estimate of the maximum temperature difference for endothermic and athermic reactions (if this difference does not exceed ~ 30 ° C) and for exothermic reactions (if it does not exceed ~ 8 ° C). Above these values, although inaccurate, the approximate formulae may still be useful in warning of large temperature errors in a TG experiment.

INTRODUCTION

An important source of error in kinetic data obtained by TG is the difference between the recorded temperature and the reaction temperature inside the sample. The effect of such errors on kinetic data has been studied by various authors [1–4]. Relatively small errors in temperature measurement may result in large errors in the kinetic parameters determined: reaction order, activation energy, and pre-exponential factor. They may also affect the assignment of reaction mechanism.

The temperature error may be a result of (i) an external temperature difference, between furnace and sample outer temperature, if the temperature is recorded at the furnace, and/or (ii) an internal temperature difference, between outer sample temperature and actual reaction temperature. The first kind of error can often be avoided: it is necessary simply to record the temperature in the immediate vicinity of the sample rather than at the furnace.

The internal temperature difference is more difficult to measure. The sample may be too small for the insertion of a thermocouple, or such

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insertion may affect the weight measurement. An alternative is to reduce the sample size until the results do not vary: this however may not be feasible or practicable. On the other hand, the change in kinetics as a function of sample size may be attributable to effects other than thermal (e.g. diffusion).

Where the temperature error cannot be avoided or measured, it is useful to be able to calculate it, in order to assess the validity of the results. A solution of the set of equations which describe the simultaneous heat transfer and reaction kinetics is not analytically possible; the numerical solution, on the other hand, is complex and requires a computer program. Pokol et al. [5] used dimensional analysis to develop an expression for the estimation of the temperature error due to heat of reaction in a spherical sample. The error estimated by this formula was compared with that estimated by a somewhat simplified computer model of the simultaneous heat conduction/reaction. The objective of this work is to find a more general formula for estimating the maximum temperature difference inside a sample in a TG experiment.

GENERAL MODEL FOR HEAT TRANSFER AND REACTION WITHIN A SOLID SAMPLE

Consider the reaction

$S_1 \rightarrow \gamma S_2 + (1-\gamma)G\uparrow$

where S_1 is the the solid reactant, S_2 is the solid product, G is the volatile product and γ is a 'stoichiometric' parameter which is unity if no volatiles are produced and zero in a volatilization reaction with no solid residue.

Temperature differences created within the sample in a temperature programmed TG experiment involving the above reaction are a result of (i) heat conduction within the sample, (ii) heat generated by reaction, and (iii) heat carried out of the sample by volatiles (if any) produced by this reaction. A model which describes these phenomena, analogous to several models in the literature [6–10], consists of the equations below. Sample volume is assumed constant throughout the reaction. Although the model is unidimensional, it is applicable to spheres, infinite cylinders and infinite slabs, depending on the geometric parameter b ($b = 2$, 1 and 0, respectively).

Enthalpy balance

$$\frac{\partial(\rho C_{ps}T)}{\partial t}\,\mathrm{d}V = \frac{\partial}{\partial r}\left(k\frac{\partial T}{\partial r}A\right)\mathrm{d}r - \frac{\partial}{\partial r}\left(M_{\mathrm{g}}C_{p\mathrm{g}}AT\right)\mathrm{d}r - \left(H_{\mathrm{r}}r_{\mathrm{c}}\right)\mathrm{d}V \qquad (1)$$

where A is the transfer area (perpendicular to r) (m^2), $C_{p\mathrm{g}}$ is the specific heat of the volatiles (kJ $\mathrm{kg}^{-1}\mathrm{K}^{-1}$), C_{ps} is the specific heat of the sample (kJ

$\mathrm{kg^{-1}K^{-1}}$), H_r is the enthalpy of reaction (kJ $\mathrm{kg^{-1}}$ of S_1 at a reference temperature of 0 °C), k is the sample thermal conductivity (kW $\mathrm{m^{-1}\ K^{-1}}$), M_g is the mass flux of the volatile pyrolysis products (kg $\mathrm{m^{-2}s^{-1}}$), r is the distance from the sample centre of symmetry (m), r_c is the rate of reaction (kg $\mathrm{m^{-3}s^{-1}}$), t is time (s), T is the solid temperature (K), V is the sample volume ($\mathrm{m^3}$), and ρ is the sample density (kg $\mathrm{m^{-3}}$).

Chemical reaction

$$-\frac{\partial \rho_1}{\partial t} = r_c = \rho_1 k_0 \exp(-E/R_g T) \tag{2}$$

$$\frac{\partial \rho_2}{\partial t} = \gamma \rho_2 k_0 \exp(-E/R_g T) \tag{3}$$

where E is the activation energy (kJ $\mathrm{kmol^{-1}}$), k_0 is the pre-exponential factor ($\mathrm{s^{-1}}$), r_c is the rate of reaction (kg $\mathrm{m^{-3}s^{-1}}$), R_g is the gas constant (kJ $\mathrm{kmol^{-1}K^{-1}}$), and ρ_i is the density of S_i (kg $\mathrm{m^{-3}}$).

Material balances (solid/pyrolysis gas)

$$-\left(\frac{\partial}{\partial t}\right) \mathrm{d}V = \frac{\partial (M_g A)}{\partial r} \mathrm{d}r \tag{4}$$

with

$\rho = \rho_1 + \rho_2$

Boundary conditions

For $t = 0$, for all r

$$\rho_1 = \rho_0 \tag{5}$$

$$\rho_2 = 0 \tag{6}$$

$$T = T_0 \tag{7}$$

$$M_g = 0 \tag{8}$$

where ρ_0 is the initial solid density (kg $\mathrm{m^{-3}}$). For $r = 0$, for all t

$$\frac{\partial T}{\partial r} = 0 \tag{9}$$

$$M_g = 0 \tag{10}$$

For $r = R$, $t > 0$

$$T = T_f \tag{11}$$

where R is the solid radius or half-thickness (m) and T_f is the recorded temperature. This last boundary condition corresponds to the assumption that the recorded temperature is equal to the outer solid temperature, i.e. there is negligible heat transfer resistance between the sample and the recording/controlling thermocouple.

Geometry

Equations (1) and (4) may be simplified using

$$\frac{dA}{dr} = \frac{b}{r}\frac{dV}{dr} \tag{12}$$

The system of eqns. (1)–(12) above is not analytically soluble. It was solved using the Crank–Nicholson method [7,8,11–13]. Details are given by Alves [14].

APPROXIMATE EXPRESSIONS FOR THE MAXIMUM INTERNAL TEMPERATURE DIFFERENCE

An order of magnitude expression for the temperature difference between the centre and the outer boundary of a sample (sphere, infinite cylinder or infinite slab) is

$$\Delta T = [T(r=R) - T(r=0)] \simeq \frac{R^2}{2(b+1)k}\left[C_{ps}\beta\rho(t) + r_c(t)H_r\right] \tag{13}$$

where β is the heating rate (K s^{-1}).

Equation (13) is not generally valid. A first condition of applicability (one usually verified) is that the experiment is long enough for the difference between the external temperature and the initial temperature to be considerably larger than ΔT, i.e.

$$T(r=R,\ t) - T(r=R,\ t=0) = \beta t \gg \Delta T = T(r=R,\ t) - T(r=0,\ t) \tag{14}$$

Expression (13) can be 'derived' for slab geometry by integrating eqn. (1) under rather drastic assumptions, namely: the convection term is negligible; r_c is constant; and $\partial T/\partial t$ is constant and equal to β. These assumptions are often unreasonable. Yet, as will be shown, eqn. (13) is a good estimate in most cases pertinent to TG, particularly to give the maximum temperature difference created during a complete TG experiment, rather than the difference as a function of time. For this purpose, two situations must be distinguished.

Moderately exothermic reaction

If the reaction is moderately exothermic, the negative enthalpy of reaction partly cancels the error due to slowness of inward heat transfer and the maximum temperature difference occurs for zero reaction rate, hence

$$\Delta T_{\max} = [T(r=R) - T(r=0)]_{\max} \simeq \frac{R^2 C_{ps} \beta \rho(t=0)}{2(b+1)k} \tag{15}$$

This is applicable if

$$| r_{\mathrm{c}_{\max}} H_{\mathrm{r}} | < 2 C_{ps} \beta \rho(t_{\max}) \text{ and } \beta t \gg \Delta T_{\max} \tag{16}$$

where $r_{\mathrm{c,\,max}}$ is the maximum rate of reaction, which can be obtained from the thermogram, and ρ $(t_{\max})$ is the sample density at the time of maximum reaction rate, $t_{\max}$.

Endothermic and highly exothermic reactions

In the case of all endothermic reactions and of highly exothermic reactions, the maximum temperature difference occurs around the time of maximum reaction rate. In this case

$$\Delta T_{\max} \simeq \frac{R^2}{2(b+1)k} \left[C_{ps} \beta \rho(t_{\max}) + r_{\mathrm{c,max}} H_{\mathrm{r}} \right] \tag{17}$$

For an exothermic reaction this happens if

$$| r_{\mathrm{c,max}} H_{\mathrm{r}} | > 2 C_{ps} \beta \rho(t_{\max}) \text{ and } \beta t \gg \Delta T_{\max} \tag{18}$$

ASSESSING THE APPROXIMATE EXPRESSION(S)

The maximum ΔT between the sample outer surface and its centre obtained through the simplified expressions [eqn. (15) or (17)] was compared with the result of model simulation [numerical solution of eqns. (1)–(12)]. This was done using different values of the most influential parameters: half-thickness R; the enthalpy of reaction H_{r}; geometry (slab or sphere); activation energy E; and pre-exponential factor k_0. E and k_0 were not independently varied: they were kept related to each other by a compensation effect of isokinetic temperature 601 K, which is typical of pyrolysis of lignocellulosic materials. The variable parameters were varied within the limits shown in Table 1. The cases considered are therefore within a matrix involving three geometries × seven enthalpies of reaction × two sets of kinetic parameters (high and low activation energy) × several diameters between 0.5 and 5 mm. The other parameters were kept constant, with values shown in Table 1. Devolatilization of 50% of the material is assumed.

TABLE 1

Value or expression for parameters used in the model

Parameter	Value or expression
ρ_0 (kg m^{-3})	1000
C_{ps} (kJ kg^{-1}K^{-1})	2.0
C_{pg} (kJ kg^{-1}K^{-1})	2.0
k (W m^{-1}K^{-1})	0.100
γ	0.5
β (°C min^{-1})	5
R (mm)	0.5–5
b	0, 2
E (kJ mol^{-1})	80, 400
k_0 (s^{-1})	$\exp[(E-25900)/5000]$
H_r (kJ kg^{-1})	−1000, −500, −100, 0, 100, 500, 1000

Figure 1 compares the maximum ΔT calculated by simulation and that estimated through eqn. (17) for endothermic and athermic reactions. Deviations from the 45° line correspond to errors in estimating with eqn. (17). It can be seen that eqn. (17) gives very good estimates for temperature differences up to 30°C.

Figure 2 compares the maximum ΔT calculated by simulation and that estimated through eqn. (15) or (17) [depending on conditions (16) and (18)] for exothermic reactions. The estimating expressions have a more limited

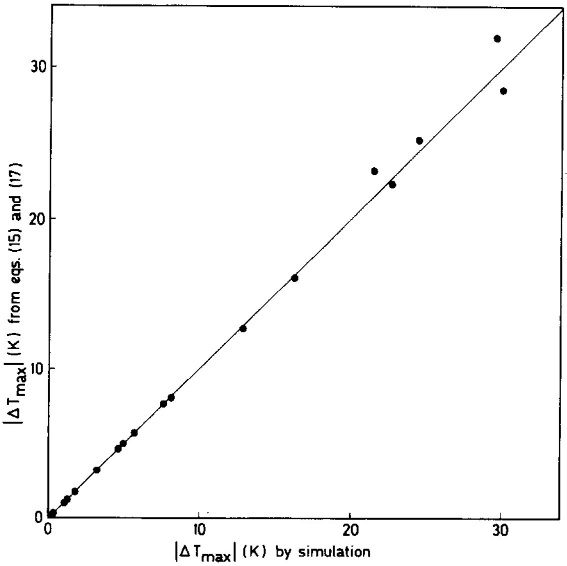

Fig. 1. Maximum temperature difference within a sample in a TG experiment: estimated using eqn. (17) vs. calculated by simulation. Endothermic reaction.

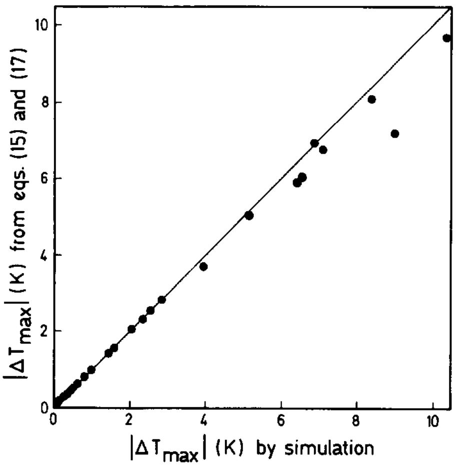

Fig. 2. Maximum temperature difference within a sample in a TG experiment: estimated using eqn. (15) or (17) vs. calculated by simulation. Exothermic reaction.

validity range, particularly at higher activation energies. This is due to the runaway temperature phenomenon, which may mean a very quick completion of reaction for exothermic reactions of high activation energies. Nonetheless, it may be said that the estimating expressions give a good estimate up to a temperature difference of ~ 8 ° C, and give a 'fair warning' of important temperature gradients above this.

CONCLUSIONS

Expression (15) or (17) (depending on specific conditions) gives a very good estimate of the maximum temperature difference between the sample outer surface and its centre in thermal analysis experiments if this difference is lower than 30 ° C, for endothermic reactions, or lower than 8 ° C, for exothermic reactions. As gradients as large as these are usually unacceptable in TG, it may be said that these expressions are useful for quantitative *T* calculation in most of the useful TG experiments.

Even above their limits of validity, the estimating expressions still give a fair warning of the existence of important temperature gradients in a temperature programmed TG experiment.

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LIST OF SYMBOLS

A	transfer area (perpendicular to r) (m^2)
b	geometric parameter (= 0 for infinite slab, 1 for infinite cylinder, 2 for sphere)
C_p	specific heat ($kJ\ kg^{-1}K^{-1}$)
E	activation energy ($kJ\ kmol^{-1}$)
H_r	enthalpy of pyrolysis at 0 ° C ($kJ\ kg^{-1}$)
k	solid thermal conductivity ($kW\ m^{-1}K^{-1}$)
k_0	pre-exponential factor (s^{-1})
M_q	mass flux ($kg\ m^{-2}s^{-1}$)
r	linear dimension in the direction of heat and mass transfer (m)
R	solid half thickness (m)
r_c	rate of reaction ($kg\ m^{-3}s^{-1}$)
R_g	gas constant ($kJ\ kmol^{-1}K^{-1}$)
t	time (s)
T	solid temperature (K)
V	solid volume (m^3)

Greek letters

β	heating rate (s^{-1})
γ	stoichiometric coefficient
ρ	solid density ($kg\ m^{-3}$)

Subscripts

f	reactor
g	gaseous/volatile products
i	refers to species i
max	maximum
s	solid
0	initial
1	solid reactant
2	solid product

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