Journal of Thermal Analysis, Vol. 49 (1997) 1089-1096

PULSED BED CALORIMETRY
A jump in speed and sensitivity

S. Walter, A. Hadj Mebarek and S. Diyani

Ecole Nationale Supérieure de Chimie de Mulhouse, 3, Rue A. Werner
F-68093 Mulhouse, France

Abstract

Conventional calorimetry has always the difficulty of choosing between near to equilibrium working conditions and high thermal ramp rates. Thus, either the transport phenomena and sample homogeneities are good but the signals become weak due to thermal losses, or the signals are sharp, but strong gradients across the sample lead to chemical and thermal heterogeneities. The described pulsed fluidized bed technique, by strongly stirring the sample, allows good sample homogeneities even at high ramp rates. Moreover, the permanently regenerated cover gas allows as well a good heat transfer towards the thermocouples as a constant atmosphere composition leading to very precise onset temperatures.

Keywords: calorimetry, fluidized bed, hyphenated, MDSC, spectrometry

Introduction

For conventional thermo-analytical purposes, one generally tries to obtain as close as possible to equilibrium conditions, since the thermodynamic control of the evolved reactions leads to easy to interpret signals. But under such conditions, no significant changes take place in the sample, equilibrium conditions being defined as leading to no macroscopic energy and matter transfer. Thus, the signals remain weak. The signal to noise ratio becomes bad, so that only the use of far from equilibrium techniques can overcome such problems.

But by working far from equilibrium, severe gradients appear, so that the sample is no longer well-defined : the signals become more intense, but several reasons can limit the reaction rate, particularly the heat transfer towards the sample as well as the total amount of matter in the sample. The limitation becomes a kinetic one, which is often badly controlled, due to the thermicity of the reaction itself.

Our new device suggests some partial solutions of the above mentioned problems.

Theoretical considerations

Although equilibrium temperatures are interesting to work at, the lowering of thermal ramp rate required therefore results in lowering the peak value (Fig. 1) of the expected signal (the area of which is nearly constant), generally consisting of heat exchange or matter transfer. When not considering systems being blocked by

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

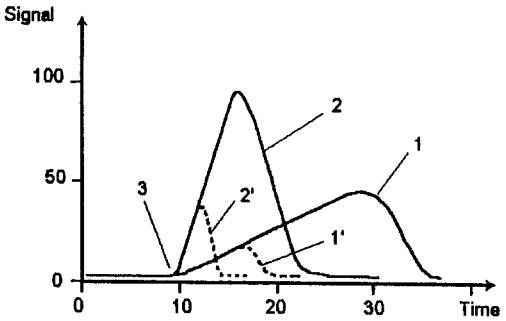

Fig. 1 Shape of signals as a function of sample size and thermal ramp rate: (arbitrary units); 1) signal with low ramp rate; 1′) same signal with smaller sample; 2) signal with double ramp rate; 2′) same signal with smaller sample; 3) onset

kinetic hindrance even far from the equilibrium conditions, the position of signal peak depends essentially on sample size (Fig. 1, 1′, 2, 2′). The onset temperature is much better defined. But the behavior of the sample strongly varies in time:

First, it is generally the heat flow reaching the sample which defines the observed reaction rate during the initial steps leading to a signal. The available heat flow can result as well from external heating (oven) as from internal heat of reaction. During the following steps, when a constant thermal ramp rate is applied to the sample, the reaction speed increases until there is no longer enough matter instead of matter enough in the sample in order to allow speed increasing: the peak value is reached, then the signal decreases and finally disappears when the whole sample has been transformed. The transfer of heat towards or inside the sample as well as the transfer of eventually evolved products result in gradients, which are not always well-defined (Fig. 2).

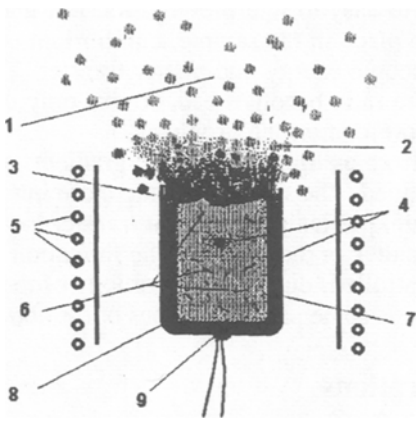

Fig. 2 Gradients arising from transfer phenomena: 1) Gas phase showing heat and matter gradients; 2) Evolved gases; 3) Sample surface; 4) Heat gradients in the sample (locally starting reaction and edges); 5) Oven heating resistors; 6) Retained liquids; 7) Wall of the sample holder; 8) Bottom of the sample; 9) Thermal sensor

For trace analysis, close to equilibrium conditions may result in total loss of the signal corresponding to minor species, the signal becoming smaller than the noise level.

To solve this problem, several points have to be taken into account: thermal analysis measures heat or mass exchanges between the sample and its environment. Generally, the resulting flows are not directional, so that the sensors just get a small part of the theoretical signal, especially when they are located, as it is commonly done, at the bottom of the sample holder (Fig. 2): convection phenomena and the eventually evolved gases draw the energy flow away, upwards, far from the thermal sensor, resulting in poor sensitivity.

Thus, our first aim was to direct precisely the characteristic energy and matter flows towards the sensors and to reduce as much as possible all losses taking place in conventional devices.

On the other hand, the heat transfers required to bring the systems the energy they need in order to undergo a transition result in gradients near the sample holder walls. These relatively long range gradients (several mm), creating thermal heterogeneities in the sample give rise to peak broadening. Gradients not only result from heat transfer from the oven, but can also be generated by locally starting reactions in a sample showing low thermal conductivity.

Experimental

Therefore (Fig. 3), we developed a fluidized bed technique: the heat is no longer tansferred to the sample across the crucible walls by conduction, but directly led to the sample by the fluidizing gas. This time, the heat transferring gradients become as small as the fluidized particle size: the macroscopic gradients of conventional techniques have been replaced by microscopic gradients.

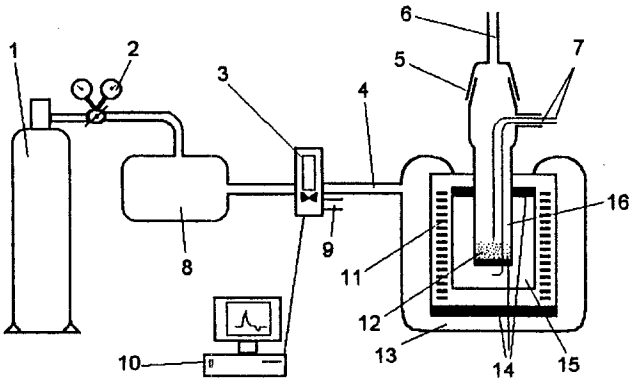

Fig. 3 Pulsed bed calorimeter: 1) Gas cylinder; 2) Pressure reducer; 3) Double electrovalve with bypass; 4) Cell gas inlet; 5) Glass stopper; 6) Gas outlet to spectrometers; 7) Differential thermocouples; 8) Low pressure gas tank; 9) Gas release; 10) Computer; 11) Heating resistor; 12) Pulsed fluidized bed; 13) External heat recuperator; 14) Coarse sintered glass filters; 15) Internal heat recuperator; 16) Thermoanalytical cell

Since the energy transfer requires time constants decreasing as the square of the sample size, by replacing the crucible size by a more than ten times smaller particle size, one requires less than one hundred times smaller gradients to tranfer the same energy in the same time.

So, we could develop a far from equilibrium working system, which can be applied each time the sample is a powdered one.

In order to allow high ramp rates, stirring of the sample is obtained by means of the fluidized bed. The first prototype of such a device has been presented two years ago [1]. The initial problems correlated with permanent fluidization have been solved by a pulsed technique. This way, instead of using badly-defined working conditions, changing from equilibrium conditions to kinetic limitation, we reach either a purely kinetic limitation of the transition reactions occurring in the sample when an inert gas is used for fluidization or thermodynamic control when all evolved gases are simultaneously present around the sample by a careful control of their partial pressures in the fluidizing gas.

The high thermal homogeneity of the sample gives rise to sharp peaks with precise onsets even at high temperatures ramp rates. The high transition speeds correlated with high thermal ramp rates result in easy to detect signals, even for minor species. To reach this result, it is essential that the thermal profile in the pulsed bed calorimeter is as close as possible to the ideal conditions shown by Fig. 4: the gas volume being pulsed has to be approximatively the same as the sample volume. The internal heat recuperator (15, Fig. 3) has approximatively the same volume. Under such conditions, the only way for heat to be evacuated from the sample is the fluidiz-

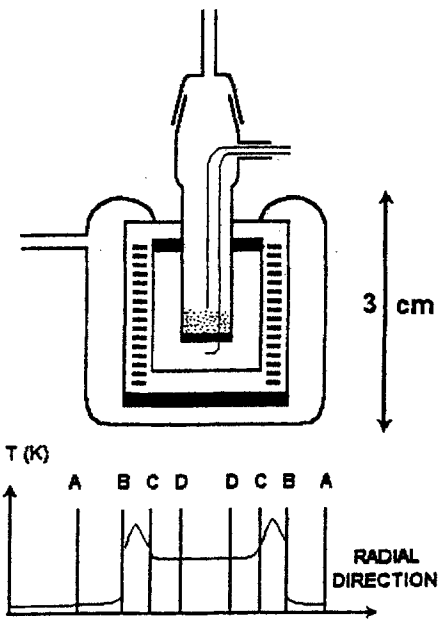

Fig. 4 Radial thermal gradients: 1) Heat flow; A) External wall; B) External heater wall; C) Internal heater wall; D) analytical cell wall

ing gas. Thus, the temperature difference observed in the fluidizing gas across the sample can be evaluated by following equation:

$$\Delta T = [\Delta H(dn/dt)\Delta t]/[mC_p] \quad (1)$$

ΔT: differential gas temperature across the sample; $[mC_p]$: total heat capacity of a gas pulse: can be lowered by decreasing the volume of the fluidizing pulse and by choosing a low specific heat capacity fluidizing gas; ΔH: enthalpy of the undergoing reaction; (dn/dt): reaction speed:

$$(dn/dt) = n_0[f(T)](1-\alpha) \quad (2)$$

n_0: initial amount of reacting species; $[f(T)]$: temperature speed function of the reaction (Arrhenius' or more complex); $(1-\alpha)$: remaining percent of initial species, decreasing to zero while the transition is going on.
Δt: time interval between two fluidizing gas pulses: can be increased as far as compatible with sufficient time (and thus temperature) resolution of the transition.

Further, a main advantage of this technique is that it allows perfect drying of the sample before thermal investigation: due to capillary effects, traces of water may be retained in the sample. This can result in drastic changes of the properties observed for some trace species present at intergranular water-sensitive grain boundaries: the presented system, Hg^{2+} in sodium or potassium iodide, is a typical example of such a behavior. The observed signals, corresponding to a true binary system, are completely different from those observed by conventional techniques, due to the water-containing corresponding ternary system.

In conventional ovens, the heat is transferred to the sample containing crucible by natural convection or conduction. Radiative heat transfer becomes important at high temperatures. The sample is thus heated up through the sidewalls, the bottom and the top of the crucible (Fig. 2) Inside the crucible, the sample is generally powdered, so that it includes at least approximatively 25% vol. of air (or another cover gas). Such small volumes of air result in low thermal conductance inside the sample. Thus, a strong thermal gradient appears across it. Moreover, when an exothermal reaction starts locally in the sample, the generated heat is difficult to evacuate and may therefore lead the sample to run away, sometimes starting from local hot points as shown by 4, Fig. 2. Therefore, our first aim was to evacuate the heat created by the transformations taking place in the sample.

The fluidized bed technique presented at ESTAC 6th [1], solved efficiently this problem. But in order to be stable, fluidized beds require a minimal size of about 4 cm. This results in important required sample sizes (up to several grams). Since such amounts of samples are not always available, our first trend was to reduce the sample size. On the other hand, the strong fluidizing air flow (several $dm^3\ min^{-1}$) led to high heat capacities of the gas phase around the crucibles. Since most of common gases exhibit a constant pressure heat capacity of about 30 J $(K\ mol)^{-1}$, our first prototype could not measure the thermal effects. The device had to be coupled to an atomic absorption spectrometer or to another hyphenated technique in order to control the sample transformations.

Moreover, fine dust particles had to be filtered off: in order to avoid contamination of the coupled analytical instruments. Since numerous evolved particles were very reactive, they were stopped by adsorption on the filter surface, leading to signals much lower than expected by theory.

So our trend was multiple:
1) to reduce the air flow
2) to reduce the sample size
3) to suppress the filter
4) to reduce the thermal losses.

1) The first point could not be reached by simply reducing the air flow, since thus we would have lost the fluidizing properties of the gas. But short pulses of a well suited gas could overcome this problem. The above mentioned instabilities do not appear this way.

2) The sample size was reduced to a few tenth of a gram. The gas pulses just lift by its own height the whole sample which settles then down again to its initial position.

3) Between two pulses, the sample is allowed to settle, so that filtering off the dust becomes useless.

4) The thermal losses were reduced by transferring directly the heat produced electrically around the sample by the fluidizing gas (Fig. 3): all thermal losses through the sidewalls are driven back to the sample at the next gas pulse by means of the buffer volume 15, Fig. 3.

Results and discussion

The heart of the device described by Fig. 4 is just a few centimeters high. The volume of the internal reactor is about 5 cm^3. The heating of the fluidizing gas has to lead to heat gradients as close a possible to the ideal curve shown by the lower part of Fig. 4. The only way the heat is exchanged by the sample is the pulsed gas. Short square-shaped pulses (the gas bypass 9, Fig. 3 enables a square-shaped end of pulse) of about 1 cm^3 are produced by an electrovalve opening the bypass within a few hundredth of a second after the opening of the main valve feeding the reactor. The gas pulse, transferring the whole heat content the sample releases directly towards the thermocouple, leads to high sensitivities. Thus, one must think energies, not power as for conventional techniques: the heat is accumulated in the sample between two pulses and then transferred towards the thermocouple. The smaller the volume of the gas pulse, the higher its temperature change. The time between two pulses is one to ten seconds: it has to allow settling of the sample, which requires a minimum time depending on particle size. On the other hand, the interval between two pulses should not be too long since temperature resolution would become bad. In order to reach good sensitivities, very fast thermocouples have been used (Thermocoax, 40 $\mu V/°C$, 0.25 mm diameter, time constant: 3 ms). A Hewlett-Packard analog to digital converter allows a computer to select the highest differential temperature measured during the gas pulse. Figure 5 has been obtained with the experimental device on hand of a well known system: traces of mercuric iodide diluted in

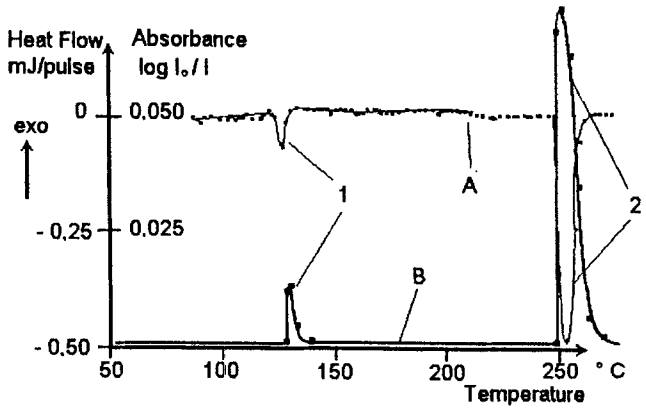

Fig. 5 Compared results of pulsed bed calorimetry and hyphenated atomic absorption: Sodium iodide sample (200 mg) containing 100 ppm Hg (0.02 mg) (0.1 μmol) in a glass device. A) pulsed bed calorimetry; B) atomic absorption; 1) solid-solid transition of HgI_2; 2) Melting of HgI_2

an alkali iodide matrix: HgI_2 undergoes an allotropic transition at 129°C and melts near 250°C [2–4].

By conventional techniques, the crucible sidewalls can induce disturbing reactions: gold or aluminium crucibles cannot be used for this purpose, since they induce decomposition of mercury salts. DSC carried out by a conventional Setaram DSC 111 calorimeter led to poor signals disappearing in the noise level. Moreover, retained water (capillary effects between the sample crystals) led to decomposition signals of iodomercurate due to the presence of water, the expected [4] signals of mercuric iodide remaining absent.

To the contrary, by the pulsed fluidized bed technique, the water being dried off, the mercuric iodide is formed back and becomes easily observable due to the high ramp rate and the correlated instantaneous energies to be detected during the gas pulse. The evolved gas phase, led to an atomic absorption spectrometer gives rise to strong atomic absorption signals. It is important to notice that the relative signal intensities of pulsed bed calorimetry and atomic absorption are quite different: the yield of atomization is not directly dependent on the thermal effects.

Conclusion

Pulsed bed calorimetry can be used as a far from equilibrium working technique. It allows an excellent thermal sample homogeneity and thus high ramp rates, up to several tens of degrees per minute. The sensitivity can be adjusted by the periodicity and the volume of each gas pulse. For thermodynamic investigations, it requires a well defined gas composition, and one has to remember that, if the applied gas does not contain ALL compouds the studied transition yields, this technique just measures kinetic speeds and NOT equilibrium temperatures. Thus, this technique being

more based on kinetics, DSC being more based on equilibria, both are complementary and should be used together in the future in order to get the best possible knowledge of the studied species. Moreover it is particularly well adapted for coupling with spectroscopic methods [4]. To the end, since temperature modulation is very easy to obtain this way due to the fast response of the heater as well as the short range diffusion distances (typically a few tenth of micrometers instead of a few millimeters by conventional techniques), this could be an excellent alternative to overcome the sample limited speeds observed in modulated DSC (MDSC) one has to take into account when conventional devices are operated.

References

1 S. Walter, F. Bloc and A. Hatterer, Flow injection coupled with Thermal Analysis: a ppb level detection method for trace contaminant determination: application to alkali metal systems, 6th European Symposium on Thermal Analysis and Calorimetry, Grado, 11–16 (9) 1994.
2 S. Walter, V. Mougenel and A. Hatterer, Analusis, 15 (1987) 486.
3 R.C. Weast, Handbook of Chemistry and Physics, 56th ed., CRC Press, Cleveland, 1975–76, D 73, B 249.
4 S. Walter and A. Hatterer, Atomic absorption: another way for phase transition characterization, J. A. A. S., 9 (1994) 525.