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A new reaction calorimeter and calorimetric tools for safety testing at laboratory scale

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Abstract

Calorimetry combined with thermal analysis is an essential tool for the evaluation of thermal risks linked with chemical reactions at industrial scale. The energies of synthesis reactions or decomposition reactions as well as the heat capacities of reaction masses can be measured using such techniques. The capacity of the SETARAM differential reaction calorimeter (DRC) to determine essential safety data has been demonstrated with the measurement of heat capacities of cyclohexane and propanoic acid. Results of an industrial reaction are also presented.

Keywords: Thermal analysis; Calorimetry; Reaction calorimeter; Thermal risk; Enthalpy of reaction

1. Introduction

Thermal runaways bring about many incidents in process chemical industry and some of them produced major accidents [1]. Thermal runaways are due to disturbances of the heat balance of a reactor resulting in a very fast increase in temperature in the reactor as well as a sharp increase in pressure.

The chemist in charge of the implementation of a chemical reaction at industrial scale must know the exact potential increase in temperature and pressure in the reactor and he must simulate all the phenomena which might happen during a thermal runaway in order to design relevant protection devices (a bursting disc in a distillation column for instance).

Considering a reactor with a double jacket cooler in which a cooling fluid circulates, if a failure occurs at the inlet of the cooling jacket, cooling is stopped and the reaction cannot be controlled anymore. If an important quantity of reagent—which has not been converted yet—remains in the reactor (accumulation), this accumulated reagent will lead to an uncontrolled temperature increase. The maximum temperature of this overheating is called maximum temperature of the synthesis reaction (MTSR) and the temperature rise between the process temperature and MTSR is called "adiabatic temperature rise" (ΔT_{ad}). At this point, a secondary decomposition reaction may be triggered and lead to a further temperature increase.

A systematic examination of the phenomena occurring after a cooling failure allows to draw a so-called runaway scenario (Fig. 1), which enhances the required thermal data:

- heat of the desired reaction;
- heat of decomposition;
- heat capacity of the mixtures.

These data enable to evaluate the risk of triggering a decomposition reaction by loosing the control over a reaction.

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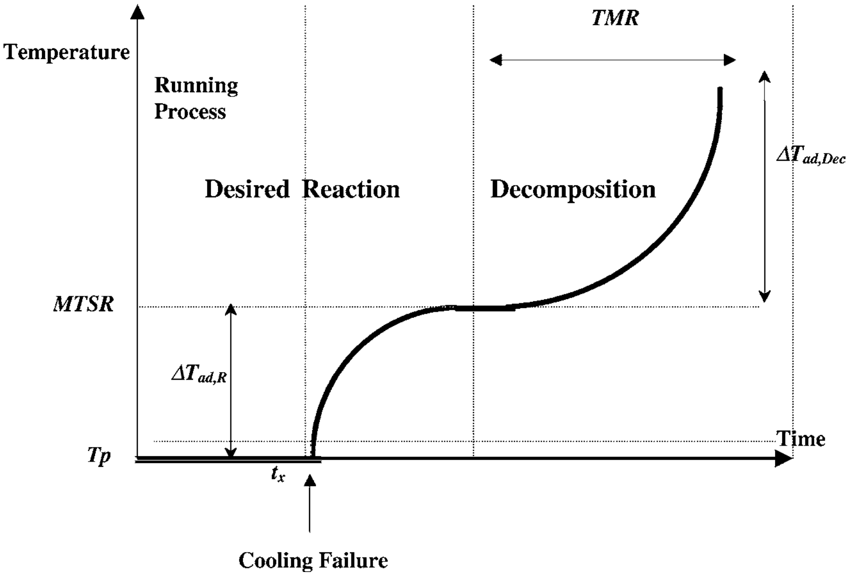

Fig. 1. Example of runaway scenario: MTSR: maximum temperature of the synthesis reaction; T_p: temperature of process; T_x: time of cooling failure; $\Delta T_{ad,R}$: adiabatic temperature rise; TMR: time to maximum rate under adiabatic conditions; $\Delta T_{ad,Dec}$: adiabatic temperature rise of the decomposition reaction.

The time to maximum rate under adiabatic conditions (TMR_{ad}) or time left before the explosion occurs can also be calculated from the heat release rate, the heat capacity and the energy of activation of the reaction. This implies a kinetic study of the reaction which is restricted to a zero-order approximation when used for safety purposes only.

One way to get the essential data about temperature, pressure and energy is the experimental determination by thermal analysis and calorimetry. Four main types of instruments can be used in a Safety Testing Laboratory: differential scanning calorimeters (DSCs), Calvet calorimeters, calorimetric reactors and adiabatic calorimeters.

In this paper, we focus on the determination of safety data for desired reactions by reaction calorimetry. Traditional reaction calorimeters use only one reaction mass having a volume of about 1 l. SETARAM has recently launched a new reaction calorimeter. A detailed presentation of this calorimeter developed in collaboration with Aventis and their Security Laboratory in Neuville S/Saône following a study done at the Swiss Institute of Safety is given hereafter [2].

2. Fast determination of the heat of reaction and heat capacity using a new reaction calorimeter called DRC

The new reaction calorimeter called differential reaction calorimeter (DRC) enables an easy and rapid determination of important thermodynamic data such as heat of reaction or heat capacity of the reaction mass. It is very easy to use due to its design very similar to a classical organic chemistry instrument. It enables to study chemical reactions in the same conditions as the ones required by classical laboratory processes. It is possible to use stirrers and a thermostated jacket and to add liquids or gases in the reactor during the measurement.

The DRC reaction calorimeter measures continuously a difference in temperature between a measurement reactor and a reference reactor. The reaction to be studied is performed in the "measurement reactor" whereas the reference reactor contains only a solvent with physical properties close to the ones of the reagents introduced in the measurement reactor.

According to the control of its surroundings, the DRC (Fig. 2) is classified as an isoperibolic calorime-

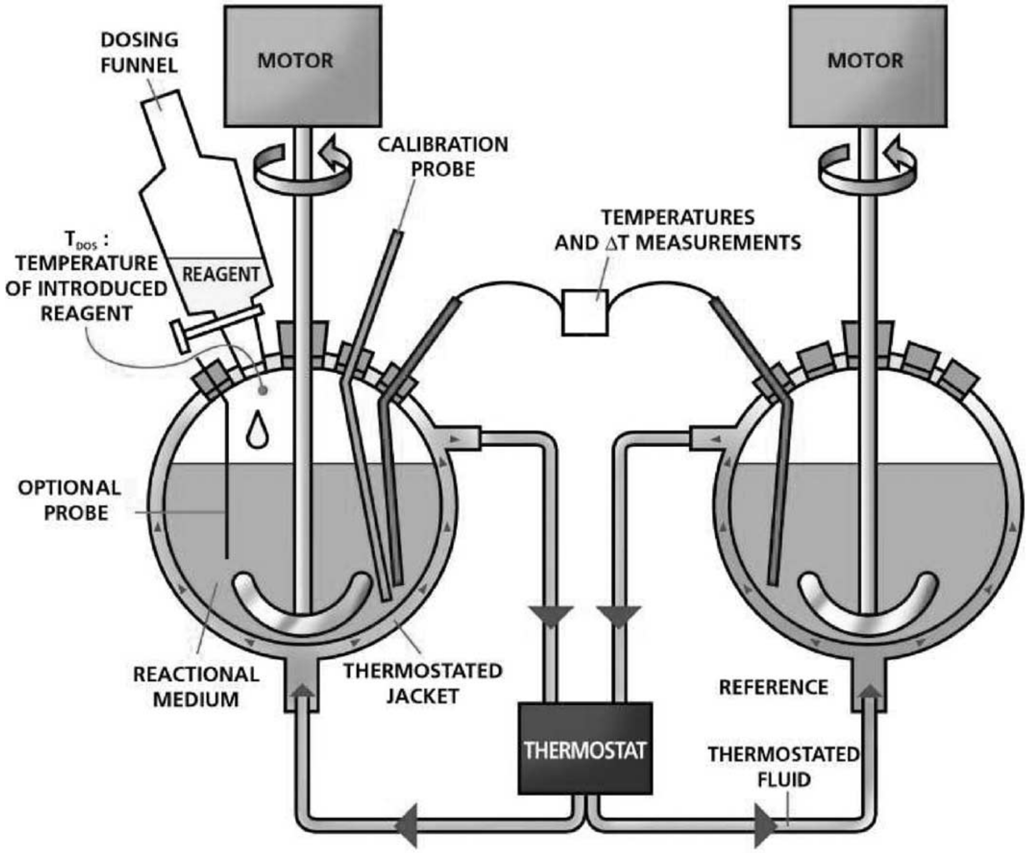

Fig. 2. Schematic view of the differential reaction calorimeter (DRC) from SETARAM.

ter [3]. Both reactors are double-enveloped spherical funnels, connected in parallel. A heat-exchanging fluid flows through the double envelops and controls the temperature of the reaction calorimeter.

The overall heat balance can be written as:

$$q_\mathrm{R} = UA(T_\mathrm{R1} - T_\mathrm{R2}) + (m_\mathrm{R} c_{p\mathrm{R}} + c_{p\mathrm{i}}) \times \frac{\mathrm{d}(T_\mathrm{R1} - T_\mathrm{R2})}{\mathrm{d}t} + \dot{m} c_{p\mathrm{dos}}(T_\mathrm{R1} - T_\mathrm{dos}) \quad (1)$$

Measuring the temperature difference between both reactors ($T_\mathrm{R1} - T_\mathrm{R2}$) enables to determine the heat release rate of the reaction, if the heat transfer (UA) and the heat capacities of the reactor contents and the inserts ($m_\mathrm{R} c_{p\mathrm{R}} + c_{p\mathrm{i}}$) are known. U is the overall heat transfer coefficient through the reactor wall to the heat carrier fluid flowing in the jacket, A the exchange area that depends on the quantity of solvent in the reactor. The term $mc_{p\mathrm{dos}}$ ($T_\mathrm{R1} - T_\mathrm{dos}$) corresponds to the heat due to the feed which may be at a different temperature (T_dos) than the reactor.

A Joule effect probe made up of a special alloy is used to calibrate the calorimeter (Fig. 3). The power used for calibration (q_C) can be set up to 10 W. If no reaction takes place and if the reactor is not fed during the calibration, the heat balance may be written as:

$$q_\mathrm{C} = UA(T_\mathrm{R1} - T_\mathrm{R2}) + (m_\mathrm{R} c_{p\mathrm{R}} + c_{p\mathrm{i}}) \frac{\mathrm{d}(T_\mathrm{R1} - T_\mathrm{R2})}{\mathrm{d}t} \quad (2)$$

The heat transfer characteristics are obtained by integration of the signal over time:

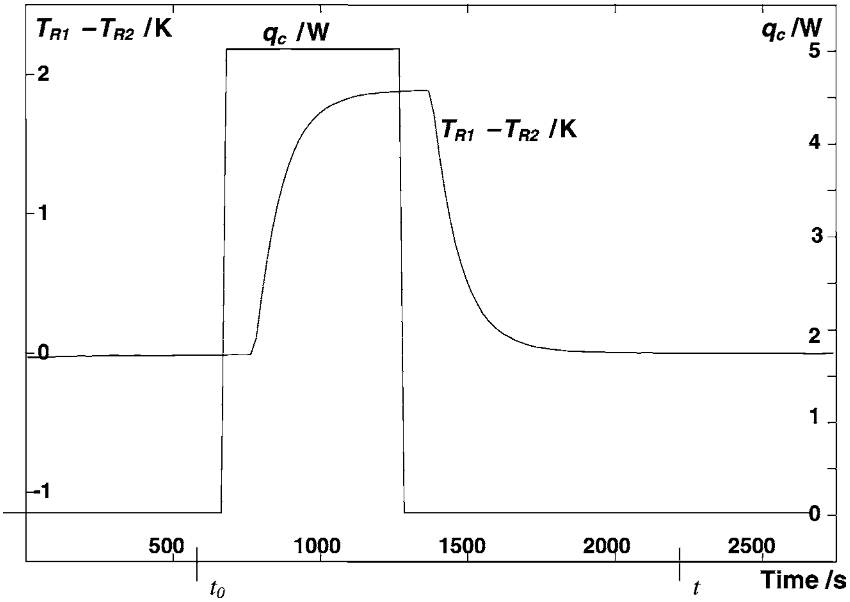

Fig. 3. Calibration of the differential reaction calorimeter by Joule effect.

$$UA=\frac{\int_0^{\infty}q_{\mathrm{C}}\,\mathrm{d}t}{\int_0^{\infty}(T_{\mathrm{R1}}-T_{\mathrm{R2}})\,\mathrm{d}t} \qquad (3)$$

The specific heat capacity of the reactor's contents can be obtained by evaluating the thermal relaxation after the calibration heater has been switched off. Eq. (2) can be integrated

$$(T_{\mathrm{R1}}-T_{\mathrm{R2}})_{(t)}=(T_{\mathrm{R1}}-T_{\mathrm{R2}})_{(t_0)}+\frac{q_{\mathrm{C}}}{UA}[1-\mathrm{e}^{-(t-t_0)/\tau}] \qquad (4)$$

with the time constant,

$$\tau=\frac{m_{\mathrm{R}}c_{p\mathrm{R}}+c_{p\mathrm{i}}}{UA} \qquad (5)$$

The heat capacity of the inserts ($c_{p\mathrm{i}}$) is determined by a calibration using a solvent with a known specific heat capacity.

Reactors are made up of glass and use glass stirrers with PTFE blades and metal inserts (temperature probe and Joule effect probe). Three kinds of double-enveloped spherical reactors of 100, 250 and 500 ml can be adapted to the reaction calorimeter. Such small volumes allow to work with small quantities of reagent which makes the calorimeter very interesting for studies performed on expensive products (pharmaceutical industry for instance).

Reactors have a central connection, which receives the agitation bearing. Reactors also have four connection pipes, which enable to fix the temperature and calibration probes as well as any other accessory (pH probe for example). Reagents are added in the calorimeter using a dosing funnel or a driven-syringe pump.

The reference reactor allows correcting the perturbations of the system in order to make possible an accurate determination of the heat of reaction and heat capacity. All phenomena, not directly related to the reaction (e.g. fluctuation of the temperature of the thermostated fluid, heat leaks through the top of the reactor, heat related to the stirring which depends on the viscosity of the reaction mass), can be corrected by using the reference reactor.

The DRC was used to measure some heat capacities of solvent, to study a well-known reaction in isothermal batch mode and an industrial reaction.

3. Heat capacities measurements of solvent

Heat capacities of different solvent where determined using Eqs. (4) and (5). The time constant τ is measured on the curve obtained during the Joule

Table 1
Heat capacities measurements

Solvent	T (K)	UA ($\mathrm{W\,K^{-1}}$)	τ (s)	$c_{p\mathrm{R}}$ ($\mathrm{J\,K^{-1}\,g^{-1}}$)	Standard deviation (%)	$c_{p\mathrm{R}}$ ($\mathrm{J\,K^{-1}\,g^{-1}}$) [4]	$\lvert(c_{p\mathrm{R}}$ [4] $- c_{p\mathrm{R}})/c_{p\mathrm{R}}$ [4]$\rvert \times 100$ (%)
Cyclohexane	313.15	1.54	125.88	1.80	0.68	1.870	3.74
Propanoic acid	313.15	1.43	179.15	2.04	0.31	2.208	7.27
Propanoic acid	333.15	1.54	172.51	2.16	0.60	2.304	6.25
Propanoic acid	353.15	1.61	170.63	2.25	0.44	2.409	6.60
Propanoic acid	373.15	1.73	165.95	2.36	0.94	2.522	6.42
Propanoic acid	393.15	2.00	146.58	2.48	1.56	2.642	6.13

effect calibration, UA is calculated using Eq. (3); $c_{p\mathrm{i}}$, which represents the heat capacities of the instruments inside the reactor has been determined previously also by Joule effect calibration using water inside the reactor, $c_{p\mathrm{i}}$ is equal to $55\,\mathrm{J\,K^{-1}}$ and is independent of the temperature.

Heat capacities of cyclohexane and propanoic acid at different temperatures were obtained using 100 ml of product in each reactor. Results are summarized in Table 1. We obtained an average agreement of about 6% between the measured values and the literature values.

4. Example 1: Hydrolysis of acetic anhydride

4.1. Reaction

The reaction studied—the hydrolysis of acetic anhydride (Fig. 4)—is a classical reaction to characterize calorimeters. It is a fast reaction well suited for checking the dynamic response of a calorimeter. It has been studied in batch mode using the DRC and the 250 ml reactors.

Acetic anhydride was obtained from FLUKA (Fluka 45830, puris. p.a. ACS ≥ 99.5%). Deionized water was used.

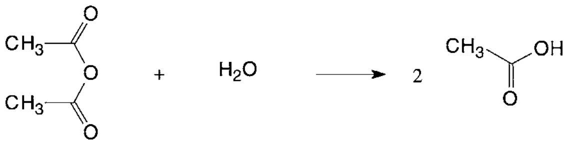

Fig. 4. Reaction scheme of the hydrolysis of acetic anhydride.

4.2. Experimental procedure and results

The reaction has been performed in isothermal batch operation at three different temperatures 283.15, 298.15, and 313.15 K. The reactor is thermally equilibrated at working temperature and contains only the solvent: 150 g (8.33 mol) of water. A heated dosing funnel maintained at the temperature of the experiment was used in order to introduce 12 g (0.12 mol) of acetic anhydride in one portion. The reference reactor contains 160 g of water which is almost equal to the final reaction mass in the working reactor. Under such conditions symmetry is maintained between both reactors.

The evolution of the working reactor temperature in function of time enables to follow the reaction progress qualitatively, i.e. the temperature returns to its initial value (baseline) after about 45 min at 313.15 K. The reaction enthalpy is obtained by integration of the temperature difference with time using the Joule effect calibration performed at the end of the experiment. The results are summarized in Table 2. A measured curve at 313.15 K is presented in Fig. 5.

The average value is $-\Delta H_{\mathrm{R}} = 57.9\,\mathrm{kJ\,mol^{-1}}$ with a standard deviation of 0.67%. This value compares well with values from literature: $-\Delta H =$

Table 2
Measured enthalpy of reaction for the hydrolysis of acetic anhydride

T (K)	Enthalpy of reaction ($\mathrm{kJ\,mol^{-1}}$)
283.15	−57.6
298.15	−57.7
313.15	−58.3

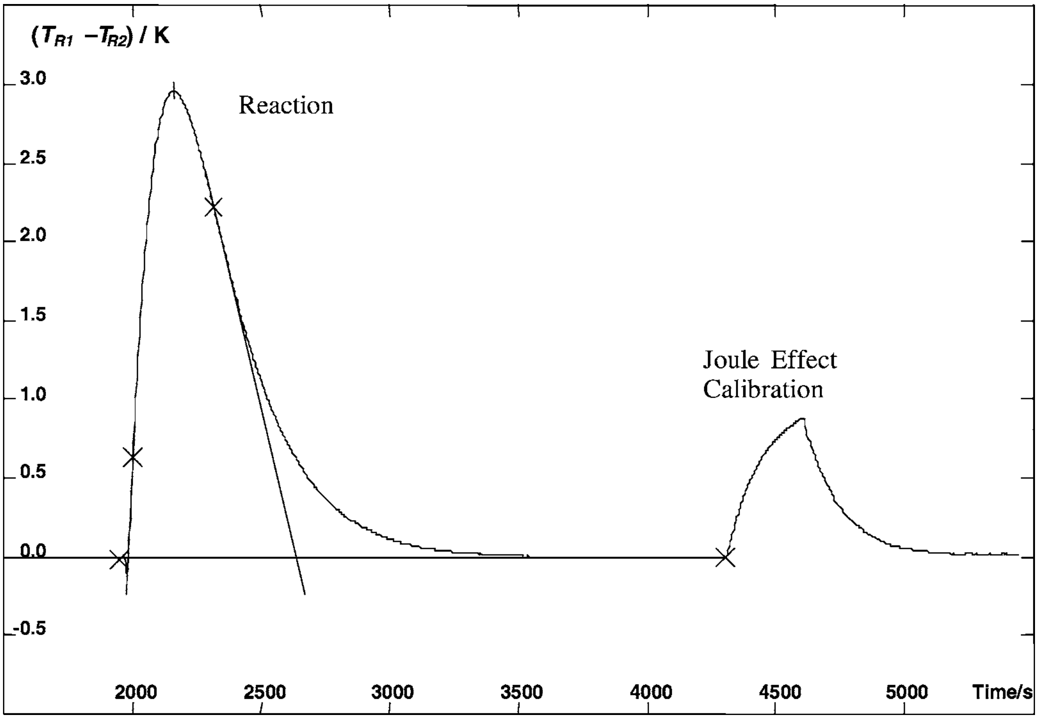

Fig. 5. Measured curve of the hydrolysis of acetic anhydride with water at 313.15 K.

60.4 kJ mol^{-1} between 288.15 and 308.15 K [5] and $-\Delta H = 58.3$ kJ mol^{-1} at 303.15 K [6].

For this relatively fast reaction, the differential reaction calorimeter gives reproducible results with a good agreement with the literature data.

5. Experimental study of an industrial chemical reaction

The reaction studied is used on an industrial scale and is the synthesis of a Grignard reagent (Fig. 6). Thirty-six grams of tetrahydrofuran (THF) and 57.5 g of toluene where placed in the reference reactor. Thirty-six grams of THF, 11.5 and 6.0 g of magnesium were placed in the measurement reactor. Reaction was studied at 313.15 K. Four millilitres of a solution of 42.75 g of alkylbromobenzene in 46.0 g of toluene were added. A first strong exothermic effect is obtained (Fig. 7). The rest of the solution of alkylbromobenzene (76 ml) is added slowly by means of a driven-syringe pump during about 1 h.

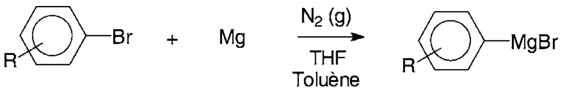

Fig. 6. Industrial reaction: synthesis of a Grignard reagent.

Heat of reaction obtained is equal to $\Delta H_R = -261.7$ kJ mol^{-1}. This value is corrected by the heat of dosing which is due to the temperature difference between the reaction mass and the added reactant. This value ΔH_{dos} is equal to 9.3 kJ mol^{-1} and was obtained by means of the temperature measurement of the alkylbromobenzene and toluene introduced in the reactor. Heat capacity of the mixture after reaction is equal to $c_{pR} = 1.4$ J g^{-1} K^{-1}. ΔH_R, ΔH_{dos} and c_{pR} are used to calculate the adiabatic temperature rise during the reaction by means of the following equation:

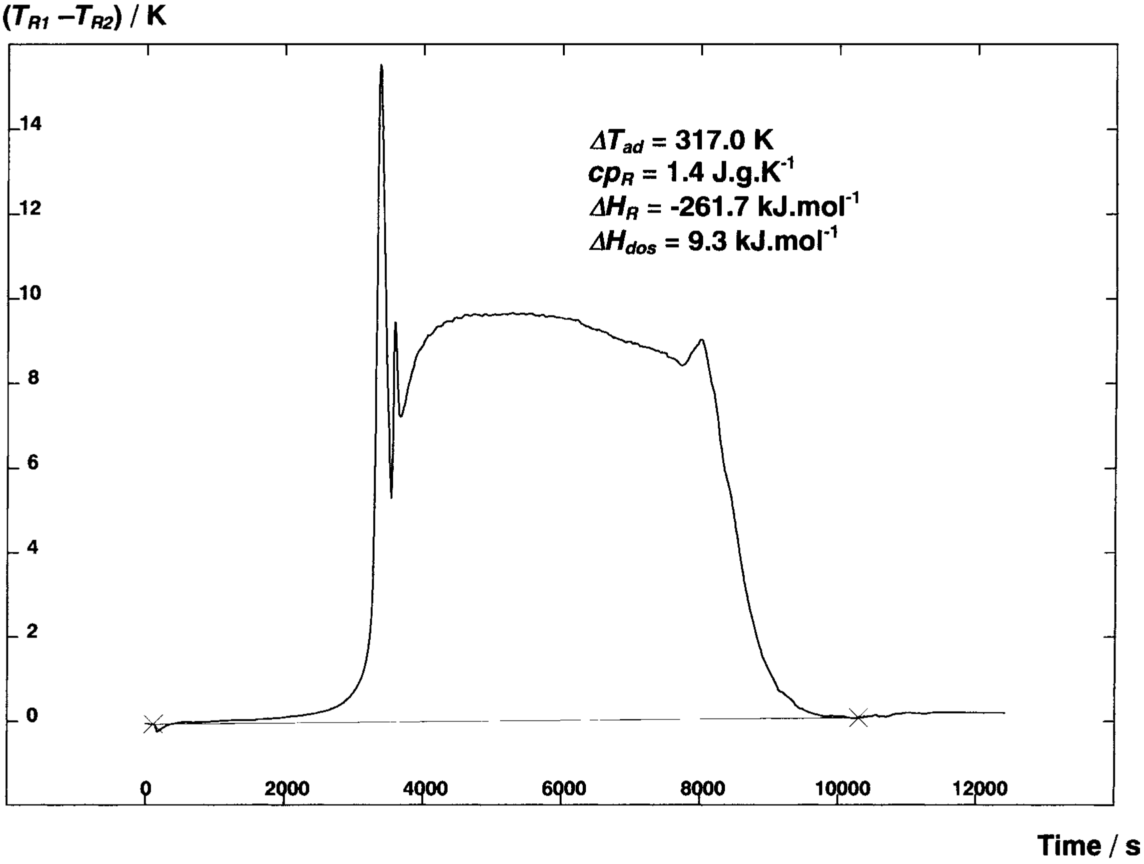

Fig. 7. Measured curve of the industrial reaction at 313.15 K.

$$\Delta T_{\text{ad,R}} = \frac{N_A |\Delta H_R|}{m_R c_p} \qquad (6)$$

N_A is the mole number of alkylbromobenzene and is equal to 0.250 mol, m_R the total mass and is equal to 142.25 g. The adiabatic temperature rise is equal to $\Delta T_{\text{ad,R}} = 317\,\text{K}$.

6. Conclusion

The examples shown in this paper, hydrolysis of acetic anhydride and heat capacities measurement of cyclohexane and propanoic acid illustrate the performance of the new DRC reaction calorimeter. This reaction calorimeter makes possible the determination of heat of reaction, ΔH_R and heat capacities, c_{pR} of reaction masses and the calculation of adiabatic temperature rise, ΔT_{ad} and maximum temperature of synthesis reaction.

An industrial reaction, synthesis of a Grignard reagent was presented. It is a very exothermic reaction and the adiabatic temperature rise calculated is 317 K. It means that if this reaction is produced at industrial scale and if there is a failure in the cooling system of the reactor where the reaction takes place, the corresponding adiabatic increase in temperature can lead to an explosion and a big disaster. Therefore, this example shows that data about temperature and heat of reaction obtained by reaction calorimetry are very useful and important for thermal hazard evaluation.

The new calorimeter (DRC) presented here is one of the tools which can be used for safety studies. It can be used as a screening tool in an organic synthesis laboratory or in a development laboratory and it is especially well suited for a fast and low-cost determination of the thermal parameters of chemical reactions.

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