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Comparison of the Results from Six Calorimeters in the Determination of the Thermokinetics of a Model Reaction

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Abstract

This paper deals with the comparison of experimental results from several types of commercially available calorimeters: a screening calorimeter (DSC), a Calvet calorimeter (C80), a reaction calorimeter (RC1), and various pseudo-adiabatic calorimeters (VSP 2, ARSST, and Phi-Tec 1). One exothermic reaction was selected as a case study: the esterification of acetic anhydride by methanol, a system which has been well studied in the literature. This reaction is put to the test in the six calorimeters under similar operating conditions. The objective of this series of tests is to obtain the thermo-kinetics of the reaction with each apparatus and compare the results. The goal is to determine which calorimetric method can be used (or not be used) for what purpose with respect to the reactive chemistry hazard. This approach gives also the opportunity to illustrate and summarize the potential of the experimental tools used in a complete risk assessment of a particular chemical process. The result can also be used in the education field as a simple and complete model of a case study.

1. Introduction

The catastrophic accident of Bhopal (India) in 1984 and the toxic cloud spread on Seveso (Italy) in 1976 are often used to illustrate the potential damages, destructions and number of victims caused by a chemical process accident. From the 80's, numerous publications and studies have focused on the risk of thermal runaway in the chemical industry in order to prevent major explosion, fire and toxic dispersion (Gygax, 1988 ; Stoessel, 2008). Despite this effort and the number of risk assessment methodologies available, the reactive incidents are still a serious problem in the U.S and all over the world. For instance, more recently, in December 2007, a major accident due to a runaway reaction occurred in T2 Laboratories, Inc., a chemical manufacturer located in Jacksonville, Florida. This accident killed four T2 employees and injured 32. In the conclusions of its investigation report, the CSB confirms that the reactive incidents – such as T2 explosion – continue to occur. In this investigation, the CSB also explain that the most important thing to managing reactive chemistry hazard is to have a thorough and complete understanding of the chemistry of the process under normal operating conditions but also in the case of all potential failures of the system (CSB, 2009). Many data bases, theoretical methodologies and experimental devices are available. Moreover, it is always possible to find a process safety laboratory well equipped in calorimetric devices to test all kind of process configurations. So why is there a lack of knowledge of the thermal behavior of the chemical reactions that are carried out in the industry? One of the reasons could be that experimental studies stay obscure for the non specialists, and can represent a non negligible cost and investigation time.

The aim of this paper is to illustrate and compare how the kinetic parameters of a chemical reaction can be extracted from different calorimetric techniques commercially available. The reaction studied has been deliberately chosen as a well known chemical system: the esterification of acetic anhydride by methanol, a system which has been studied in the literature. This reaction is carried out in six different calorimeters in similar operating conditions: screening calorimeter, DSC, isothermal calorimeter, C80, reaction calorimeter, RC1, pseudo-adiabatic calorimeters, VSP, ARSST and Phi-Tec 1.

The objective of this series of tests is to obtain the thermo-kinetics of the reaction with each apparatus and compare the results. The goal is to determine which calorimetric method can be used (or not be used) for what purpose with respect to the reactive chemistry hazard. This approach gives also the opportunity to illustrate and summarize the potential of the experimental tools used in a complete risk assessment of a particular chemical process. The result can also be used in the education field as a simple and complete model of a case study.

2. Experimental methods

2.1 Chemicals

High purity methanol and acetic anhydride (>99%) were purchased from Merck.

2.2 Calorimeters

Since thermal risks of a chemical process is directly associated with the absorption or release of heat, calorimetry is a suitable tool to investigate the thermal safety of such processes. Since its inception by Lavoisier in the 18th century, a vast choice of different calorimeters, using a variety of designs and measurement principles has been developed. A fairly complete description of the design and use of these calorimeters is given in the recent publication by Stoessel [1].

One can find different ways to classify calorimetric methods: the size of the sample, the design (for example with or without reference cell), the thermal sensitivity and the way of using the heat balance. In this study, six representative calorimeters have been chosen:

- Differential Scanning Calorimeter (DSC) - The DSC 131 commercialized by Setaram measures a heat flux difference between a few milligrams of sample and a reference, placed in a same temperature controlled oven and following the same scan rate [2]. It is used to detect exothermic and endothermic behaviors: phase transitions, heat capacity, chemical reactions/decompositions, etc. The test gives the thermal power and energy released by the sample [3].
- Calvet calorimeter - The C80 commercialized by Setaram is also a differential calorimeter that may be operated isothermally or in the scanning mode as a DSC [2]. It allows to work with more important sample volumes (several grams) and shows a higher sensitivity (around 0,1 W.kg⁻¹) essentially due to the measurement principles, based on a thermocouple pile totally surrounding the cells (sample and reference). As in the DSC, the test gives the thermal power and energy released by the sample [4].
- Reaction calorimeter - The RC1 commercialized by Metler Toledo is a 2 liters laboratory batch reactor designed to carry out the procedure as close as possible to plant operating conditions in a safe environment for the worker [5]. All actions (feed, mixing, safety procedure...) are controlled by dedicated software so that the operator can stay at a safety distance. The heat released by a reaction is then calculated by measuring the difference between the reaction mixture temperature and the jacket temperature. Three temperature programmed modes are available: isothermal (reaction mixture temperature is maintained constant by controlling the jacket temperature), isoperibolic (jacket temperature is maintained constant) and adiabatic (the jacket temperature is programmed to be equal to the reaction mixture temperature). This test gives access to the thermokinetic behavior of the reaction mixture [6].

Pseudo-adiabatic calorimeters - the objective of pseudo-adiabatic calorimeters is to reproduce as close as possible adiabatic conditions by limiting the heat exchanged with the environment. They are bench scale calorimeters, which can be used for simulating the way in which exothermic runaway reactions will be likely to occur in large-scale equipment. Indeed, in industrial practice, in the case of a chemical reactor failure (agitator or cooling system unexpected shutdown for instance), the reaction medium is instantly placed in adiabatic conditions. Depending on the technology, adiabatic conditions can be reproduced either by insulating the sample, or by heating the environment of the sample. In practice, part of the heat released by the reaction serves to heat the test cell. Thus, a correction of the thermal inertia is required. The correction is made by taking into account a correction factor, called Φ -factor and expressed as:

$$\Phi = 1 + \frac{m_{\text{cell}} \cdot C_{p,\text{cell}}}{m_r \cdot C_{p,r}} \quad [\text{Eq. 1}]$$

Where m_{cell} is the mass of the test cell, $C_{p,\text{cell}}$ is the heat capacity of the test cell, m_r is the mass of the reacting sample and $C_{p,r}$ is the heat capacity of the reacting sample. Three apparatus were used in this study:

- The ARSST commercialized by Fauske uses 10 mL glass test cells. This cell is first wrapped by a cylindrical heater belt following the shape of the cell and then insulated with layers of foil and felt insulation. The test cell is then introduced in a 400 mL pressure vessel. The reaction mixture and a magnetic stirrer are introduced in the cell as well as a thermocouple. The pressure inside the vessel is measured by a pressure transducer [7].
- The VSP 2 commercialized by Fauske uses 110 mL stainless steel test cells with very thin wall which limits the thermal inertia. The test cell is placed in a first heater used to heat the sample. The assembly is then placed in a second heater, named guard heater, used to regulate the temperature around the cell. Thus the temperature around the cell is regulated to be equal to that of the reaction mixture temperature inside the cell continuously. The test cell is placed in a 4 L pressure vessel. The later and the cell have a pressure transducer. Two main configurations are possible: open and closed cell tests. When the cell is open, the pressure is the same inside the cell and in the pressure vessel. In this configuration, the gaz and vapor produced by the reacting mixture can escape from the cell to go in the pressure vessel. When the cell is closed, the pressure of the containment vessel is programmed to follow the pressure inside the test cell to avoid the explosion of the cell. In this configuration, the gaz and vapor produced by the reaction can potentially be dissolved in the reacting mixture [7].
- The Phi-Tec 1 commercialized by HEL uses 10 mL stainless steel test cells surrounded by metal guard heaters. The guard heater can track the temperature. The test cell walls are thick so as to resist a pressure up to 200 bar. Thus no pressure compensation is needed [8].

The three apparatus give access in the temperature and pressure rise in pseudo-adiabatic conditions

3. Test results

3.1 Operating conditions

The esterification of acetic anhydride by methanol was carried out with operating conditions as close as possible for the six calorimeters. A mole ratio of 1:2 with an excess of methanol was chosen. Considering the critical temperature of methanol, the maximum temperature of the tests never exceeded 240°C. Main operating conditions used for each calorimeters are summarizes in Table 1.

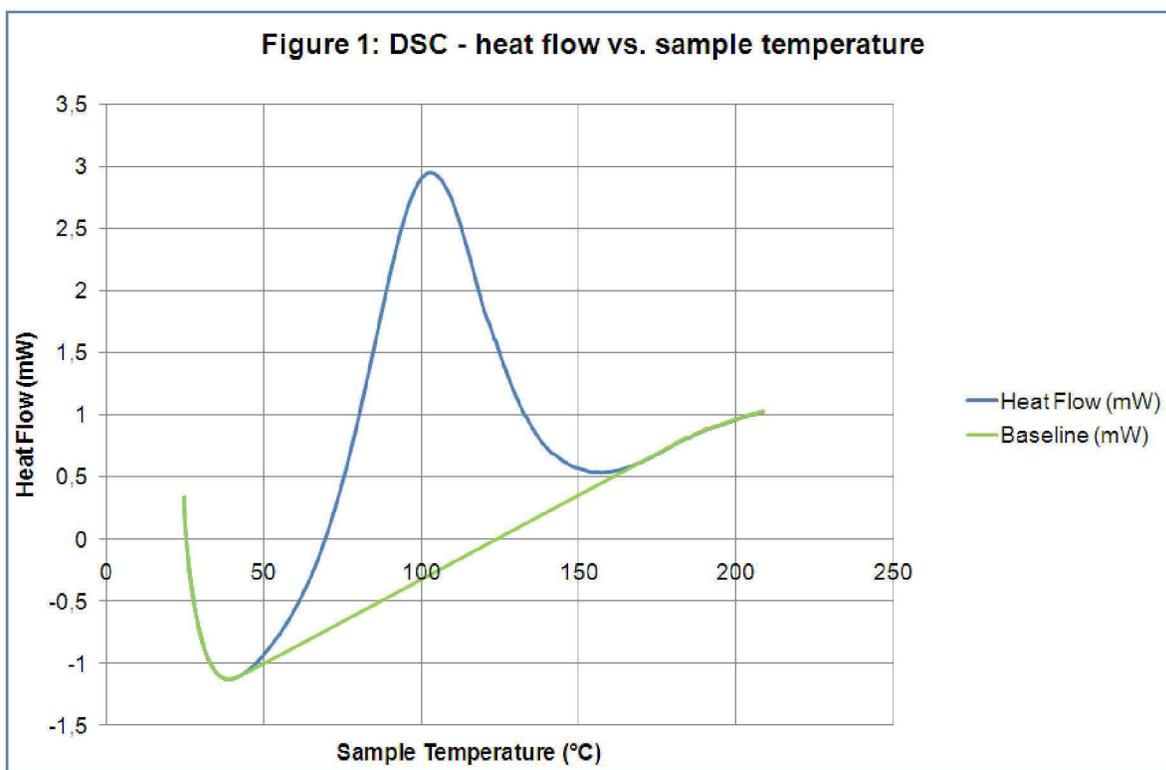
Table 1. Operating conditions

Calorimeter	Molar fraction	Test Sample	Temperature
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	Acetic anhydride : Méthanol	Mass	range
DSC	1 : 2 mol	5.33 mg	20 – 250°C
C80	1 : 2 mol	813.9 mg	20 – 250°C
RC1	1 : 0.6 mol	776.9 g	60°C
ARSST	1 : 2 mol	8.1 g	20 – 250°C
VSP 2	1 : 2 mol	74.4 g	20 – 200°C
Phi-Tec 1	1 : 2 mol	7.3 g	20 – 200°C

3.2 Differential Scanning calorimetry (DSC)

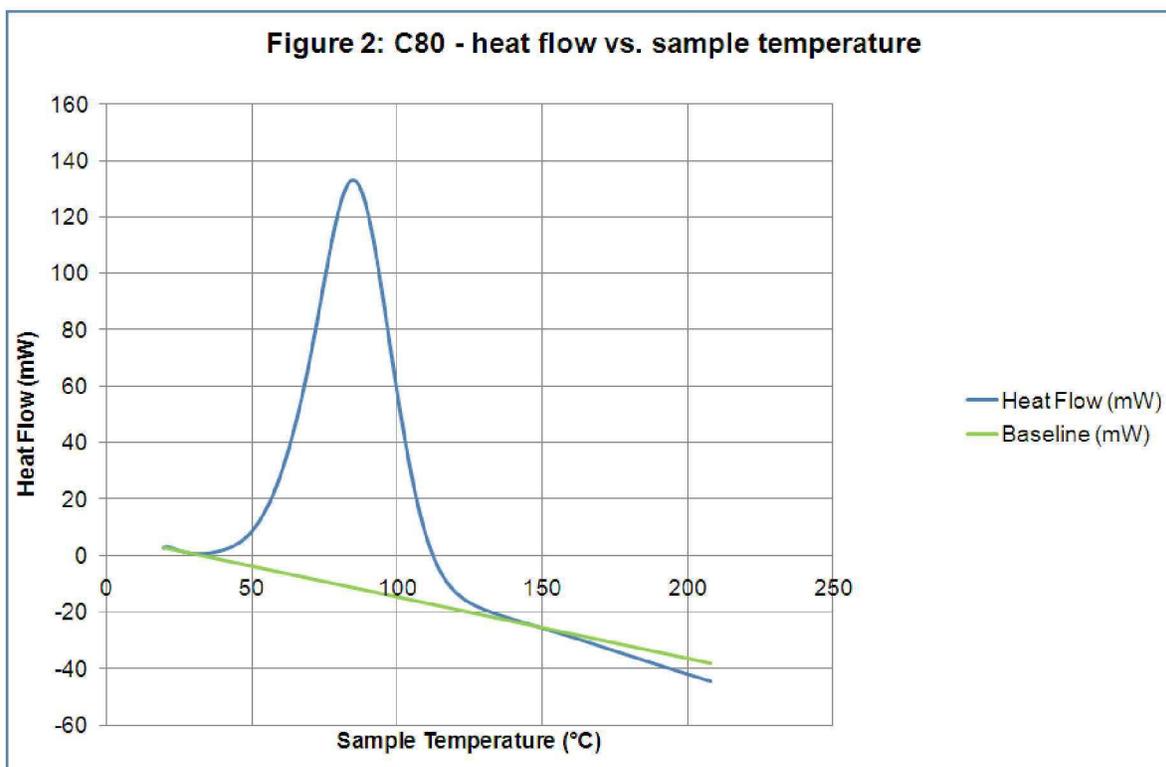
Few grams of the reactive mixture is first prepared in a 50 mL glass flask and vigorously agitated with a magnetic stirrer during 2 minutes. 5.33 milligrams of the preparation are then taken and introduced in the crucible. The latter and the reference crucible are placed into the oven and heated at 5°C/min from room temperature to 210°C. The test result gives the heat flow as a function of sample temperature (cf. figure 1). The baseline is used to integrate the heat flow and calculate the energy released by the reaction.



3.3 Calvet calorimeter (C80)

Few grams of the reactive mixture is first prepared in a 50 mL glass flask and vigorously agitated with a magnetic stirrer during 2 minutes. 813.9 milligrams of the preparation are then taken and introduced into the test cell. The latter and the reference cell are placed into the oven and heated

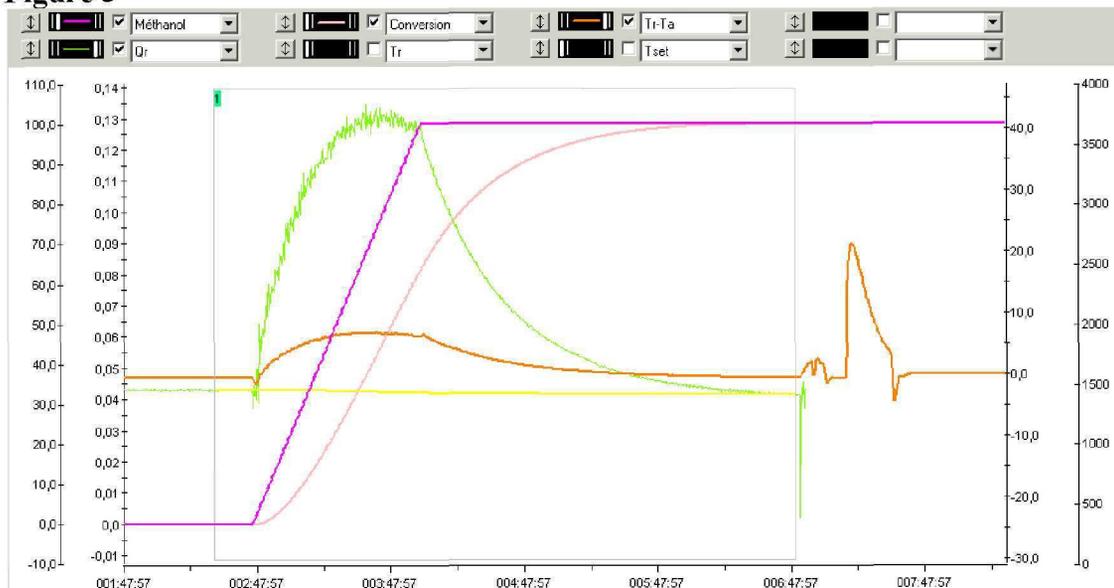
at 1°C/min from room temperature to 210°C. The test results give the heat flow as a function of sample temperature (cf. figure 2). The baseline is used to integrate the heat flow and calculate the energy released by the reaction.



3.3 Reaction calorimeter (RC1)

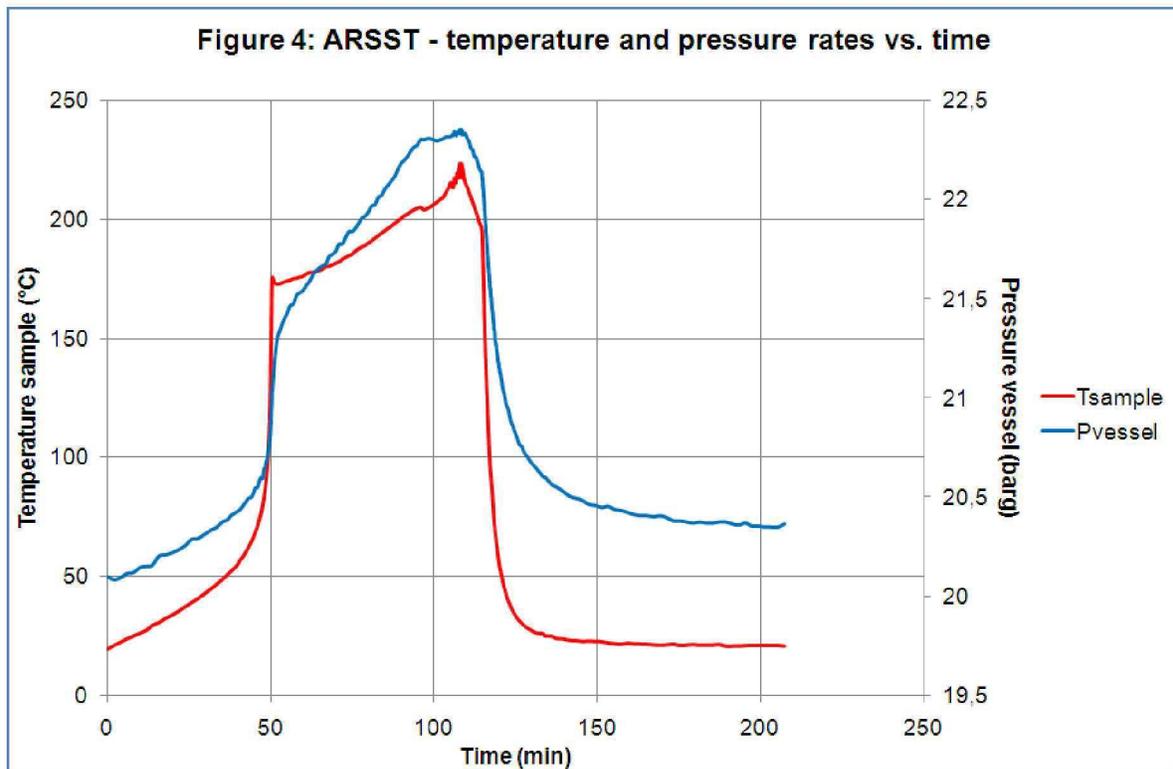
The operating procedure is more elaborated in the RC1 which is carried out at a larger scale. First of all, 648 g of acetic anhydride is introduced into the 2 liter reactor. The agitator is then started at 100 rpm. The rotation speed is chosen in order to have the temperature sensor immersed in the acetic anhydride. The product is then heated at 60°C and the reaction calorimeter is switch to isothermal mode in order to stabilize the reaction temperature at this value during the entire experiment. 128.09 g of methanol is pumped into the reactor over a period of 2 hours and 45 minutes. For safety reasons, 20% less methanol was added compared to the other experiments. When methanol is first added, the jacket temperature slightly increases in order to maintain the reaction temperature constant, which means that an endothermic effect occurs. Subsequently, the jacket temperature decreases significantly, which means that an exothermic reaction occurs. During the feeding, a light reflux appears on the reactor walls. The reaction is considered complete when the jacket temperature is exactly equal to that of the reaction temperature. During the experiment, the monitoring screen displays the jacket temperature, the reaction mixture temperature and mass of methanol introduced in the reactor. After the experiment, the software calculates the heat and mass balance to give the heat flow and the thermal conversion (cf. figure 3). The baseline is used to integrate the heat flow and calculate the energy released by the reaction.

Figure 3



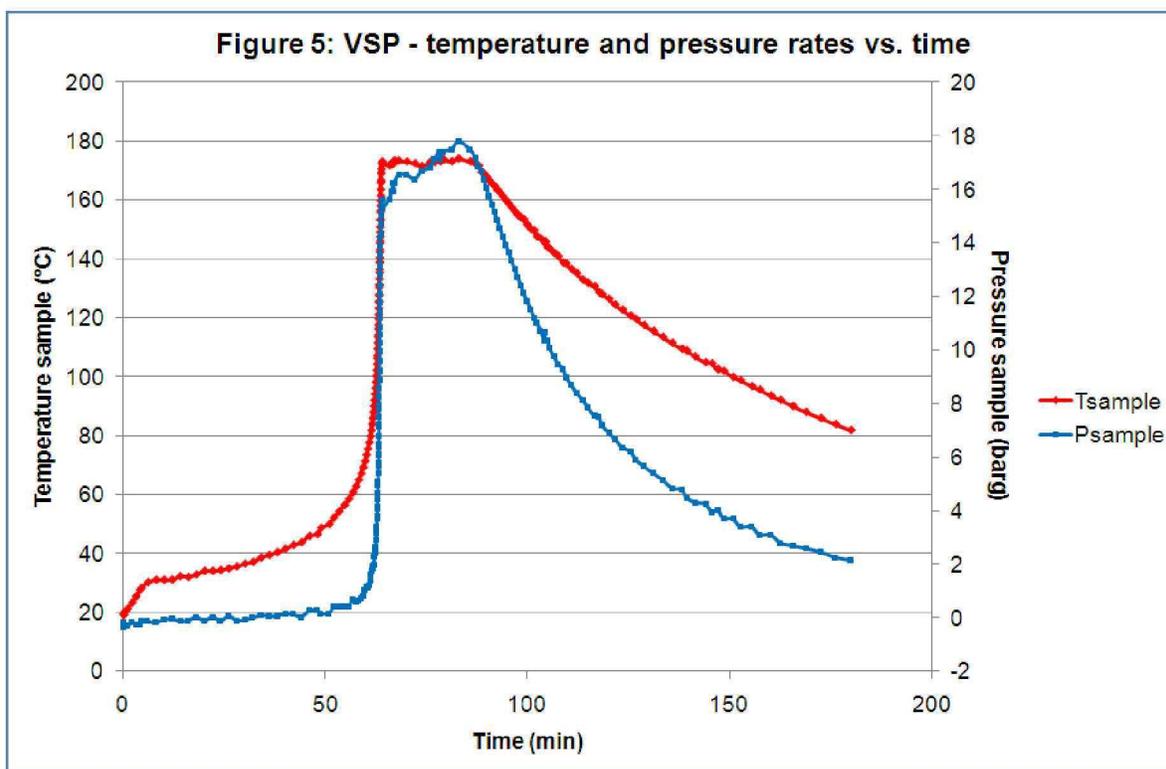
3.4 Advanced Accelerated Rate Calorimeter (ARSST)

Few grams of the reactive mixture is first prepared in a 50 mL glass flask and vigorously agitated with a magnetic stirrer during 2 minutes. 8.1 grams of the preparation are then taken and introduced in the test cell. After having wrapped and introduced the test cell in the vessel, the latter is pressurized at 20 barg to avoid the evaporation of the reaction mixture at high temperature. The heater belt is then started to heat the sample at around 1°C/min. During the experiment, the temperature of the mixture and the pressure of the vessel are recorded. When the reaction occurs, a significant temperature and pressure rise are visible. When the reaction is over, the temperature follows again the temperature rate imposed by the heater belt. The test result gives the temperature and pressure rates (cf. figure 4).



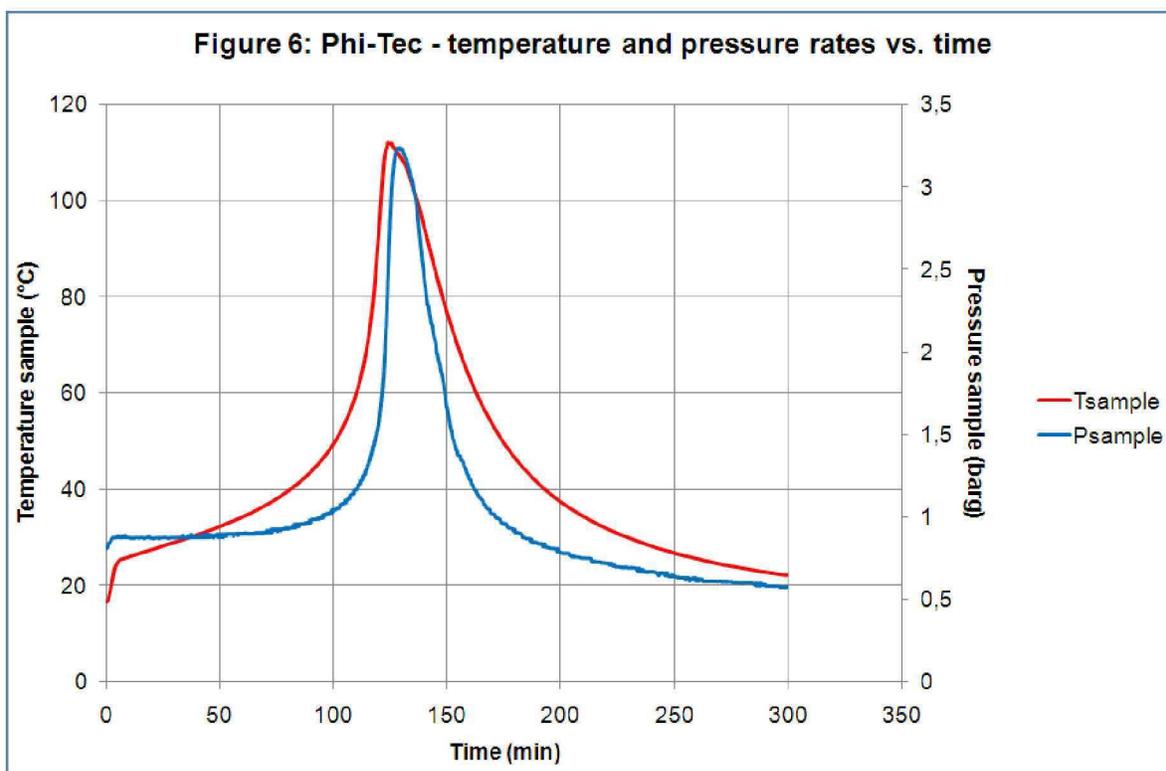
3.4 Vent sizing package (VSP)

The test is performed in closed test cell. 80 mL of the reactive mixture is first prepared, vigorously agitated and directly pumped in the test cell already placed in the pressure vessel. The reaction mixture is first heated to 28°C at around 2°C/min. The VSP is then switched to adiabatic mode to track the exotherm. The test results give the temperature and pressure rates inside the test cell (cf. figure 5).



3.4 *Phi-Tec I*

This test is performed in the closed cell test mode. 7.3 g of reaction mixture is introduced in the 10 mL test cell. The sample is then heated at around 0.2 °C/min to 250°C using the heater wrapped around the test cell. Any exotherm is detected and proceed to completion adiabatically with the guard heater tracking the sample temperature. The test results give the temperature and pressure rates inside the test cell (cf. figure 6).

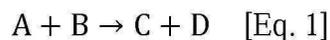


4. Kinetic calculation theory

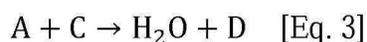
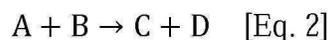
4.1 Kinetic equations

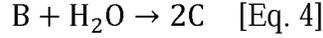
The objective is now to extract the kinetics from all results obtain from the six calorimeters. Depending on the calorimeter type, the information readily available is different: on one hand differential calorimeters (DSC, C80) and reaction calorimeter (RC1) give mainly the heat flow; on the other hand pseudo-calorimetric calorimeters give mainly temperature rate. The paragraph bellow recalls the basic theory and proposes for each case, simple equations to be used for the estimation of the kinetics parameters.

The esterification of acetic anhydride by methanol can be written:



where A is methanol, B acetic anhydride, C acetic acid and D is methyl acetate. But in reality, the reaction mechanism is more complex and several reactions may be involved. Balland and al. [9] proposed the following reaction path:





The heat production corresponds to the heat release rate by the reaction. Therefore, it is proportional to the reaction enthalpy and to the reaction rate [1]:

$$q_r = (r)V(-\Delta H_r) \quad [\text{Eq. 5}]$$

Where r is the reaction rate, V is the volume reactor and ΔH_r is the reaction enthalpy.

With two reactants, the reaction can be expressed as:

$$r = k \cdot C_A^n \cdot C_B^m \quad [\text{Eq. 6}]$$

Where k is the reaction constant, C_A is the methanol concentration, C_B is the acetic anhydride concentration and $n+m$ is the order of the reaction. The reaction constant is a function of the activation energy (E_a) and the temperature (T) according to Arrhenius:

$$k = k_0 \cdot e^{-E_a/(RT)} \quad [\text{Eq. 7}]$$

The combination of equations 5, 6 and 7 gives:

$$q_r = k_0 \cdot e^{-E_a/(RT)} \cdot C_A^n \cdot C_B^m \cdot V \cdot (-\Delta H_r) \quad [\text{Eq. 8}]$$

$$q_r = k_0 \cdot e^{-E_a/(RT)} \cdot n_A^n \cdot n_B^m \cdot (-\Delta H_r) \cdot V^{1-n-m} \quad [\text{Eq. 9}]$$

As methanol is in excess:

$$n_{A_0} = 2n_{B_0} \quad [\text{Eq. 10}]$$

And the equation of the heat release rate becomes, with x as the thermal conversion:

$$q_r = k_0 \cdot e^{-E_a/(RT)} \cdot n_{B_0}^{n+m} \cdot (2-x)^n \cdot (1-x)^m \cdot (-\Delta H_r) \cdot V^{1-n-m} \quad [\text{Eq. 11}]$$

It can also be written as a logarithmic expression:

$$\ln\left(\frac{q_r}{(2-x)^n \cdot (1-x)^m}\right) = \ln(k_0 \cdot n_{B_0}^{n+m} \cdot (-\Delta H_r) \cdot V^{1-n-m}) - \frac{E_a}{RT} \quad [\text{Eq. 12}]$$

Thus, when the heat flow and the reaction enthalpy are known, kinetics parameters can be estimated from equation 12. This is directly the case for DSC, C80 and RC1 but not for the pseudo-adiabatic calorimeters. For those, another expression can be used as demonstrated below.

The reaction enthalpy is calculated from:

$$-\Delta H_r = C_p \cdot \Delta T_{ad} \quad [\text{Eq. 13}]$$

Where C_p is the specific heat of the reaction mixture and ΔT_{ad} is the adiabatic temperature rise. For pseudo-adiabatic calorimeter, the calculation has to take into account the phi-factor (Φ):

$$\Delta T_{ad} = (T_f - T_0) \cdot \Phi \quad [\text{Eq. 14}]$$

Where T_f is the final exotherm temperature and T_0 is the exotherm onset temperature. From equation 6, reaction rate can also be written:

$$r = 2^n \cdot k \cdot C_{B_0}^{n+m} \cdot (2-x)^n \cdot (1-x)^m \quad [\text{Eq. 15}]$$

If we assume that the fractional change in temperature is a direct measure of conversion, we can write the following equations:

$$x = \frac{T-T_0}{T_f-T_0} \quad [\text{Eq. 16}]$$

$$r = 2^n \cdot k \cdot C_{B_0}^{n+m} \cdot \left(\frac{2T_f-T_0-T}{T_f-T_0} \right)^n \cdot \left(\frac{T_f-T}{T_f-T_0} \right)^m \quad [\text{Eq. 17}]$$

$$r = -\frac{dC_B}{dt} = C_{B_0} \cdot \frac{dx}{dt} = C_{B_0} \cdot \frac{1}{T_f-T_0} \frac{dT}{dt} \quad [\text{Eq. 18}]$$

$$C_{B_0} \cdot \frac{1}{T_f-T_0} \frac{dT}{dt} = 2^n \cdot k \cdot C_{B_0}^{n+m} \cdot \left(\frac{2T_f-T_0-T}{T_f-T_0} \right)^n \cdot \left(\frac{T_f-T}{T_f-T_0} \right)^m \quad [\text{Eq. 19}]$$

We obtain two expressions of k:

$$k = \frac{dT/dt}{(T_f-T_0) \cdot \left(\frac{2T_f-T_0-T}{T_f-T_0} \right)^n \cdot \left(\frac{T_f-T}{T_f-T_0} \right)^m} \quad [\text{Eq. 20}]$$

$$\ln(k) = \ln(2^n \cdot k_0 \cdot C_{B_0}^{n+m-1}) - \frac{E_a}{RT} \quad [\text{Eq. 21}]$$

The kinetic parameters can be estimated in this case from the temperature rate.

4.2 Experimental results

From DSC and C80 experiments, the integration of the heat flow gives the reaction enthalpy. The kinetic is then calculated from equation 12 by plotting $\ln\left(\frac{q_r}{(2-x)^n \cdot (1-x)^m}\right)$ versus $-\frac{1000}{T}$. The slope gives the activation energy. Different values of n and m are tested. The best combination corresponds to the best linear line obtained. Figure 7 shows an example for the calculations made from the DSC test results.

For the RC1 experiment, 20% less of methanol was added. The kinetic cannot be directly extracted with the same method.

For the ARSST, VSP and Phi-Tec experiments, the kinetic was calculated using equations 20 and 21 by plotting $\ln \frac{dT/dt}{(T_f - T_0) \cdot \left(\frac{2T_f - T_0 - T}{T_f - T_0}\right)^n \cdot \left(\frac{T_f - T}{T_f - T_0}\right)^m}$ versus $-\frac{1000}{T}$. The slope gives the activation energy. Different values of n and m are tested. The best combination corresponds to the best linear line obtained.

The calculation results are summarized in Table 2.

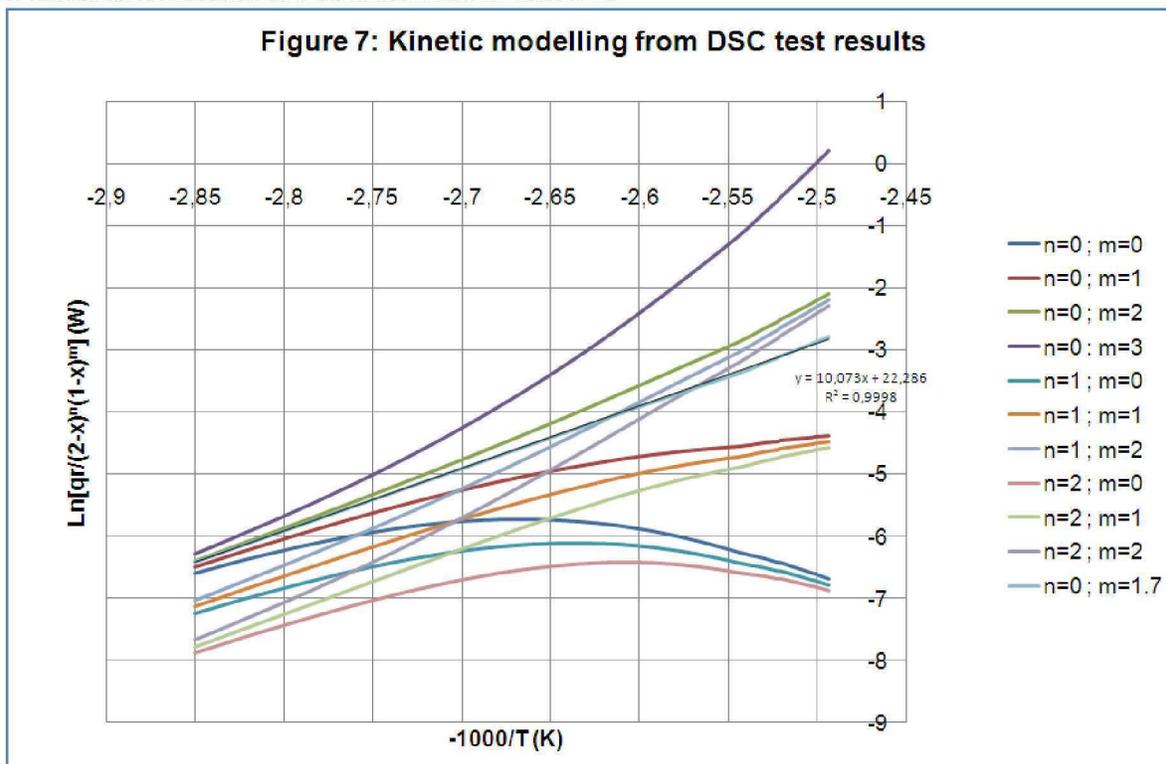


Table 2. Title of Table

Calorimeter	E_a (kJ.mol ⁻¹)	$-\Delta H_r$ (kJ.mol ⁻¹ of acetic anhydride)	n	m
DSC	83.7	57.4	0	1.7
C80	96.7	62.0	0	1.5
RC1	--	60.3	--	--
ARSST	80.2	60.7	0	1.5
Phi-Tec I	95.8	52.2	0	1.5
VSP II	81.9	59.4	0	1.5

5. Discussion and conclusion

It is possible to determine the enthalpy of reaction with the six calorimeters. With the exception of the results of the Phi-Tec I, the enthalpy of reaction determined by the different calorimetric techniques is $-60 \text{ kJ.mol}^{-1} \pm 4\%$. This value is about 9% less than that reported by Widell [10].

Comparing the results between the DSC and the C80 experiments, the onset temperature are both around 40°C and the form of the curves are similar. However, the peak temperature is lower for

the C80 experiment because of the lower heating rate, 1°C/min as opposed to 5°C/min for the DSC. The enthalpy determined by the DSC experiment is about 5% less than the enthalpy determined by the C80 experiment. In principle, C80 is more precise because of the sample size and the more precise flux meter.

For the pseudo-adiabatic calorimeters, the main difference between the VSP and the Phi-Tec I experiments is in the sample size (74 g versus 7 g) and the Φ factor. In terms of the results it can be noted that the maximum temperature attained in the Phi-Tec I experiment is substantially lower than the maximum temperature attained in the VSP (110°C versus 170°C). In order to obtain the reaction enthalpy, it is necessary to correct the adiabatic temperature rise with the Φ factor. It should be noted that the Φ factor for the Phi-Tec I apparatus is much greater than one. In the two tests the filling factor was approximately the same. However the maximum pressure is much greater for the VSP experiment (18 barg for VSP versus 2.5 barg for Phi-Tec).

The ARSST experiment is somewhat different from the two pseudo-adiabatic cited above in that the sample is heated during the entire experiment (1°C/min).

The overall adiabatic temperature rise is very close to that found in the VSP experiment. However, the pressure rise is difficult to compare to the closed cell experiments because the vapors fill the containment vessel at ambient temperature such that the vapors can condense on the walls. It is found that the pressure rise in the containment vessel is substantial and is closer to the overall vapor disengagement found in the VSP experiment.

The RC1 reaction calorimeter operates on a different principle and the only value that can be compared with the other is the enthalpy of reaction.

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