Some international references

Sanofi Aventis - France
Diosynth - Netherlands
Organon - Netherlands
Astra Zeneca - Sweden
Akzo Nobel - Netherlands
Oril Industrie, Groupe Servier - France
Astra Zeneca - UK
Syngenta - UK
Firmenich Inc - USA
Nestec - Switzerland
INERIS - France
Pfizer - USA
Institute of Safety and Security - Switzerland
Novartis - Switzerland
Synkem - France
Bayer - Germany
Hercules - USA
NAVSEA (US NAVY) - USA
The Dow Chemical Company - USA
Boehringer - Germany
Zambon - Italy
Akzo Nobel - Netherlands
Wacker Chemie - Germany
BASF - Germany
Merck - USA
Stazione Sperimentale per i Combustibili - Italy
Centre d'études de Gramat - France
Ashland Chemical Company - USA
Mitsubishi Chemicals - Japan
LG Chem - Korea
KOSHA - Korea
National Research Institute of Fire & Disaster - Japan

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Process Safety

Thermal analysis and calorimetry solutions

SETARAM Instrumentation
KEP Technologies

Excellence in thermal analysis and calorimetry

Process safety:
a challenge for everyone

The control of industrial manufacturing or transformation processes is of vital importance. Protection of personnel and the environment, as well as fundamental economic aspects, mean that the safety of such processes is a crucial issue at all levels for companies specialized in chemicals, or using chemical reactions on an industrial scale.

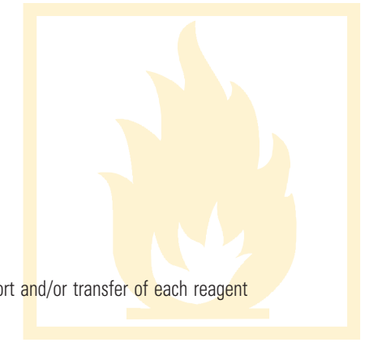
Legislation

- The European Directives Seveso I&II classify companies according to their risk threshold and oblige them to study the hazards on their sites.

- The new European regulation REACH (Registration, Evaluation and Authorization of CHemicals) applies to chemicals sold in quantities exceeding one ton. Its objective is to define and promote a "culture of process safety".

- Other types of recommendations are issued by international organization such as the IPCS (International Programme of Chemical Safety) or the WHO (World Health Organization).

What problems are encountered in process safety?



Process safety engineers on chemicals sites must:

- assess the risks (explosion, fire, etc.) associated with the conditions of storage, transport and/or transfer of each reagent involved in the process.

- select the safest operating conditions (choice of reactants, reaction temperature, type of reactor - batch, semi-batch, continuous, etc.) while at the same time ensuring that the process remains economically viable.

Thermal stability and decomposition

Before analyzing the risks associated with an operation (transport, handling, purification, reaction, etc.) the intrinsic hazards of the reactants, intermediate products and end-products involved must be assessed. Their thermal stability must be maintained within the process conditions throughout the process.

Thus, in case of thermal decomposition, the minimum critical temperature at which this is triggered and its enthalpy must be evaluated. When studying decompositions accompanied by gaseous emissions, the induced **pressure** increase must also be estimated.

But evidencing product instability is not enough to define the hazards associated with a product. The kinetics will determine the time required to trigger a decomposition **(runaway time)** and the speed of that decomposition.

pressure

runaway time

Risks associated with a process in normal conditions

The safety of chemical reactions is dependent on controlling:

- the heat produced and its removal

The heat release rate from the reaction and the capacity of the reactional system to accumulate heat must be measured and compared with the process cooling capacity.

- the gases released by the reaction

The gases emitted during a reaction can simply come from the evaporation of a solvent, a reagent, an intermediate product or an end-product of the said reaction. Non-condensable gases can also be produced by the reaction. They represent a higher risk.

The evaluation of the pressure increase induced by these phenomena enables venting systems to be dimensioned (valves, rupture disks, etc.).

abnormal functioning

Risks associated with a process in off-normal conditions

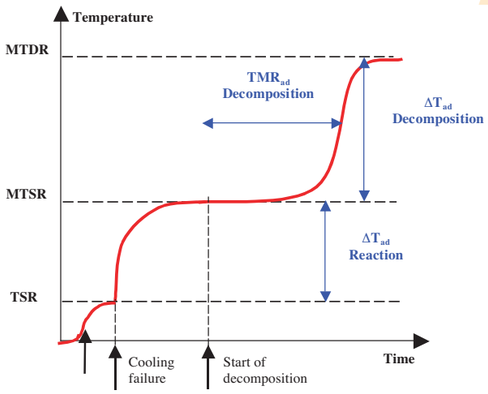
When the safest operating conditions for a process have been defined, scenarios for estimating the consequences of a shortcoming (failure, equipment **abnormal functioning**, human factors, etc.) must be devised.

In the classic case of a reactor that is subject to a cooling and stirring failure, **the accumulation of heat** exceeds the removal of heat. The reaction temperature is no longer controlled…

In order to describe such a thermal runaway scenario, the following parameters must be evaluated:
- the heat release rate provided by the synthesis reaction
- the capacity of the cooling system
- the maximum temperature increase of the system and the rate of temperature increase
- at what moment will a failure of the cooling system present the greatest risk?
- whether a secondary reaction exists
- the heat release rate provided by any such secondary reaction
- the temperature increase induced by that secondary reaction
- the time necessary for the triggering of that secondary reaction **(runaway time)**

accumulation of heat

runaway time



Example of a runaway scenario

The evaporation of a solvent, a reagent, an intermediate product or an end-product of the reaction is thermally favorable (because it is endothermic). It can nevertheless present a risk if the process is not designed to withstand high pressures.
The non-condensable gases produced by the synthesis and/or decomposition reaction represent an even greater risk.

pressure

Calorimetry
is the solution !

Calorimetry allows the measurement of the thermodynamic and kinetic data necessary for the defining and designing of safe processes.
Several types of calorimeter are used. They simulate the temperature and pressure conditions used in industrial applications.

Differential scanning calorimeter (DSC)

DSC is used to measure the heat flux difference between a reactive system and an inert "reference" system, with the two systems being subjected to the same temperature program. The differential scanning calorimetry technique requires just a few milligrams of material and is fast and inexpensive. Thanks to its temperature and pressure range, all the thermal effects associated with both the desired reaction and any secondary reactions or decompositions are detected and quantified.

Isothermal calorimeter

The isothermal approach is used to measure heats of reaction and kinetic parameters of these reactions on a few grams of sample material. It requires long-duration tests, therefore isothermal calorimeters must have a signal that remains very stable over time.
Generally speaking, as sample quantities are larger than with DSC the isothermal calorimeter can be used to study heterogeneous mixtures with an even greater resolution.

Adiabatic calorimeter

Adiabatic calorimetry allows thermal runaway phenomena to be reproduced. This approach is preferred for simulating poor conditions of heat transfer at the core of an industrial reactor, when it suffers a cooling system failure for example. In this case, all the heat produced by the reaction builds up and fuels its own auto acceleration (runaway).
Adiabatic mode is therefore considered as the most critical in process safety.

Reaction calorimeter

This term is used when the calorimeter, whatever its temperature programming mode (scanning, isothermal or adiabatic) allows the simulation of a chemical process under conditions of stirring, mixing (batch or semi batch), reflux, etc. close to industrial conditions.
This method, which generally uses cells with a capacity of 10 mL to 500 mL, makes it possible to work with material quantities that are more representative of the industrial reactional masses.

Customer testimony

If I was setting up a new process safety laboratory, I would start with a Calvet C80 calorimeter because, even if it can't solve each process safety problem, it can be used for both synthesis reactions (mixing cell) and decomposition reactions, by offering an appreciable advantage, namely pressure measurement.
I would start with a Calvet C80 calorimeter, even if it meant supplementing it later on:
- with a reaction calorimeter that would give a more representative measurement of the reactant accumulation and the heat release rate of the synthesis reaction.
- with a DSC that offers greater screening productivity (scanning rate) and a wider temperature range (>300°C).

Prof. Francis STOESSEL,
Swiss Institute for the Promotion of Safety, Basle, SWITZERLAND.

SETARAM Instrumentation
product offering **for Process safety**

SENSYS DSC: **differential scanning calorimeter**

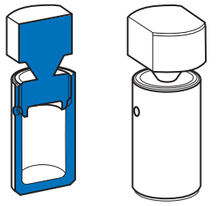
Highly modular

- Temperature range: -120 / +830 °C
- Sample weight: 1 mg to 500 mg approx.
- Uses "3D-sensor", the exclusive SETARAM Instrumentation calorimetric sensor
- **Highly modular:**
  - Sensys DSC Robot: with automatic sample changer
  - Sensys DSC HP: for high pressures
  - Sensys TG-DSC: connection to a microbalance (thermogravimetry)
- Wide range of samples and atmospheres:
  - Solids and powders
  - Liquids (corrosive liquids included)
  - Inerting conditions
  - Tests in air, in controlled humidity
- **Stability screening**

Sensys DSC

Stability screening

Special high-pressure crucibles for Sensys DSC: they have a screw-in stopper (without a seal). They withstand pressures of up to 500 bars at up to 600°C. They are equipped with a safety system that ensures compliance with European Directive CE97/23 for pressure equipment. They also exist in a gold-finish version.



High pressure crucible for SENSYS DSC HP

DRC Evolution: **differential reaction calorimeter**

- Temperature range: -80 /+150°C
- Sample weight: 50g approx. to 1kg approx.
- Uses a differential principle
  (1 measurement reactor and 1 reference reactor)
- Isoperibolic operation (control of external temperature)
- Mechanical stirring
- Controlled introduction of liquids (semi-batch reactions)
- Measurement of external signals (e.g. pH)
- Low cost
- **Screening of synthesis reactions**

DRC Evolution

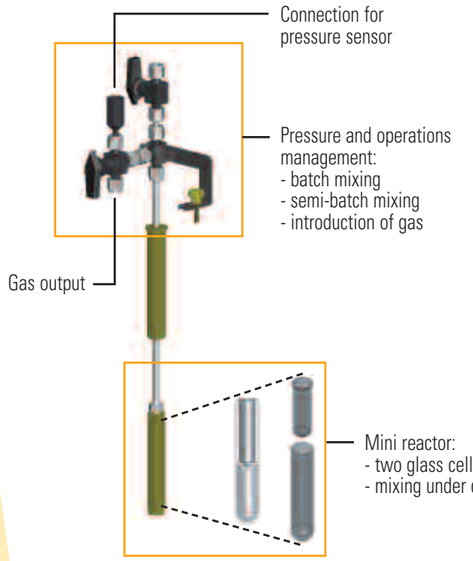
Screening of synthesis reactions

This calorimeter was developed jointly with the process safety laboratory of Sanofi-Aventis in Neuville-sur-Saône (France).

C80 Calorimeter:
reaction, isothermal and scanning calorimeter

- Temperature range: ambient / +300°C
- Sample weight: 1g to 10g approx.
- Uses 3D-sensor, the exclusive SETARAM Instrumentation calorimetric sensor
- **Pressure** controlled up to 100 bars, measured **up to 350 bars**
- Operating modes: isothermal or temperature scanning
- Numerous cells available:
  - Batch mixing
  - Controlled introduction of liquids (semi-batch mixing)
  - Gas circulation
  - Mini reactor

C80 Calorimeter



Mini-reactor for C80 calorimeter

When equipped with the SAFETY cell or mini reactor, the C80 calorimeter becomes a **highly versatile reaction calorimeter.**

This "mini-reactor" cell was developed in collaboration with the Swiss Institute for the Promotion of Safety, Basle, Switzerland.

New Accelerating Rate Calorimeter and APTAC

- **Adiabatic calorimeters**
- Temperature range: -70°C to 500°C
- Sample weight: 1g to 100g approx.
- Pressure measured up to 700 bars
- The New Accelerating Rate Calorimeter is said to be "pseudo adiabatic"
- The APTAC approaches the perfect adiabatic mode
- Available options:
  - Magnetic agitation
  - Vent sizing
  - Controlled introduction of liquids (semi-batch mixing)
  - Varyphi
- **Stability screening under adiabatic conditions.**

Adiabatic conditions

Stability screening

"New Accelerating Rate Calorimeter" (Adiabatic calorimeter)

Advanced kinetics:
Thermokinetics and Thermal Safety Software

It can happen that the calorimetric data only are not sufficient to describe the thermal behavior of a substance. Making a more detailed description requires having information of a kinetic nature.

Very rarely the investigated compounds are "pure" materials decomposing in one stage. They more generally involve reactional mediums inducing complex decomposition kinetics (multiple decompositions and/or chain reactions, autocatalysis). The use of simplified kinetic models gives results that are unsuitable for predicting the behavior of such substances over the long term. Yet such calculations are often applied in thermal stability studies, favoring excessively wide safety margins and resulting in substantial economic losses.

Our Swiss partner Advanced Kinetics and Technology Solutions (AKTS) designs, develops and updates this software. **SETARAM Instrumentation and AKTS are the sole distributors of AKTS products**.

Advanced Kinetics and Technology Solutions has developed software based on **advanced numerical techniques**. The method consists in evaluating very precisely the kinetic parameters of a given reaction, then using them to predict the progress of that reaction in **a multitude of different thermal profiles**:

- isothermal, scanning, stepwise
- temperature modulation, periodic temperature variations
- fast temperature rises (temperature shock).
- true ambient temperature profiles selected from a list of 7000 locations

Thanks to the precise input data provided by the SETARAM Instrumentation calorimeters and the precise determination of the kinetic parameters, a "Thermal Safety" module allows the **prediction** of:

- the runaway time under adiabatic conditions (TMRad) at any temperature, and the construction of a safety diagram: runaway time as a function of process temperature (TMRad = f(T))
- effects of scale, geometry, heat transfer and heat accumulation (insulation), thermal conductivity, obtained by "finite element analysis"

The combination of the SETARAM Instrumentation calorimeters and the prediction software developed by AKTS provides a unique and powerful solution for determining reaction kinetics, being fundamental in the domain of Process Safety.

Use SETARAM

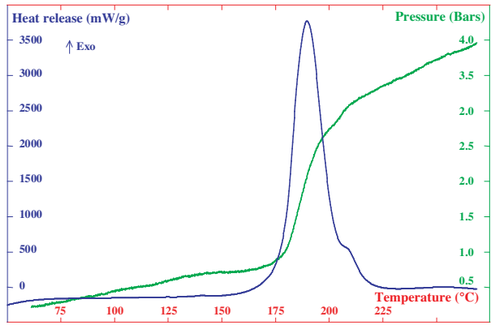
Intrumentation calorimeters for safer processes !

Thermal stability and decomposition

The thermal stability of chemical products, like that of highly energetic substances such as propellants or explosives, is particularly important during their storage and transportation. The thermodynamic and kinetic data of their decompositions must be described in detail. The minimum temperature of decomposition (onset temperature), the decomposition enthalpy, the pressure increase and prediction of behavior in adiabatic mode are obtained through a series of tests on the C80 calorimeter followed by processing with the AKTS kinetics and safety application programs.

The excellent resolution of the C80 calorimeter enables it to detect the multi-stage decomposition of a nitrocellulose and nitroglycerine-based substance. Equipped with pressure sensor cells, it can also evaluate the quantities of gas emitted and the gas release rate.

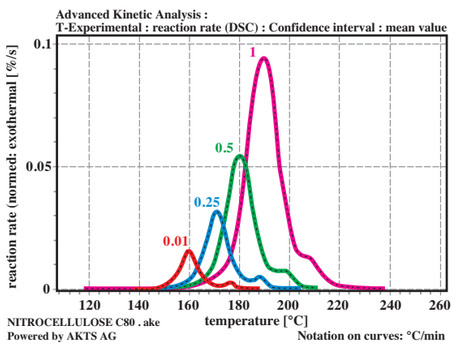
pressure



C80 : Decomposition of a nitrocellulose and nitroglycerine-based sample

The calorimetric curves opposite represent the decompositions of nitrocellulose and nitroglycerine-based samples performed at 0.10, 0.25, 0.5 and 1°C/min using the C80 calorimeter.

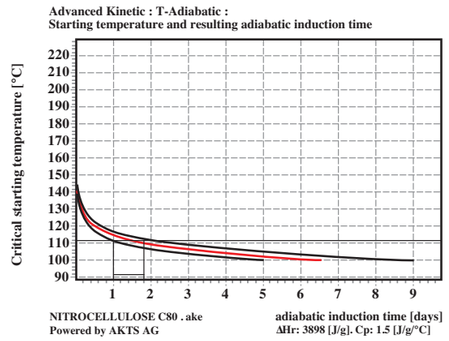
The experimental points (dots) and curves simulated by AKTS software (color lines, heating rates marked on the curves) show a perfect match.



C80 + AKTS: Decomposition of nitrocellulose and nitroglycerine based samples performed at 0.10, 0.25, 0.5 and 1 °C/min

When applied to the above system, the AKTS method allows adiabatic conditions to be predicted. The variation in the **runaway time** under adiabatic mode is plotted as a function of temperature. The critical value TMRad = 24 hours, commonly accepted as the safety limit on the industrial scale, is obtained at 114°C.

runaway time

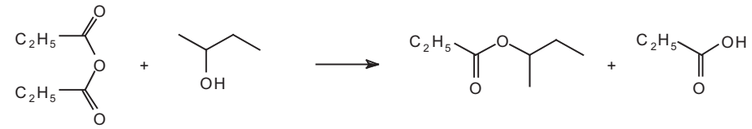


C80 + AKTS: Simulation of adiabatic conditions

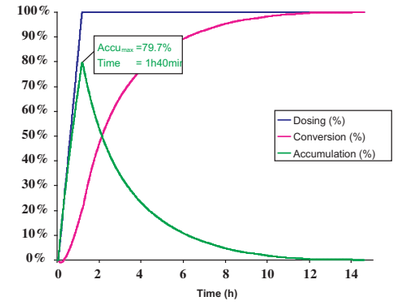
Risks associated with a process in normal conditions

The esterification of the propanoic anhydride by the 3-butanol is studied in semi-batch mode at a process temperature of 70°C. The 2-butanol is introduced into the measurement reactor using a syringe driver.

DRC Evolution: Esterification of a propanoic anhydride



Processing of the heat balance from the **DRC Evolution** enables the reagent conversion and accumulation curves to be plotted for this process. One notes the peak of 2-butanol build-up (79.7% build-up at time 1h40min), which corresponds to the potentially most dangerous situation. The reaction is slow and slightly exothermic.



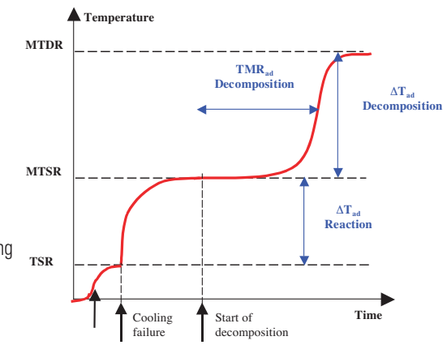
DRC Evolution: conversion and build-up of 2-butanol

Risks associated with a process in off-normal conditions

The diagram below shows an example of a classic runaway scenario: a reactor suffering a cooling and agitation failure. The failure occurs at the temperature of synthesis reaction **(TSR)**. The system is then considered to be adiabatic, and reaches its Maximum Temperture of Synthesis Reaction **(MTSR)**. An exothermic decomposition reaction can then be triggered, taking the system to the Maximum Temperature of Decomposition Reaction **(MTDR)**.

Three main parameters are measured:
- the temperature rise of the synthesis reaction (ΔTad Reaction)
- the temperature rise of the decomposition (ΔTad Decomposition)
- the induction time of the decomposition reaction (TMRad Decomposition)

There are three possible approaches:
- **use of an adiabatic calorimeter** such as the New Accelerating Rate Calorimeter or the APTAC
- **use of the C80 calorimeter** coupled with the AKTS software
- **use of the DRC** for the synthesis reaction and Sensys DSC + AKTS for the decomposition



Example of a runaway scenario