ARC accelerating rate calorimeter

(extracts from F.Stoessel, Thermal safety of chemical processes, 2nd edition, 2020, chapter 4)

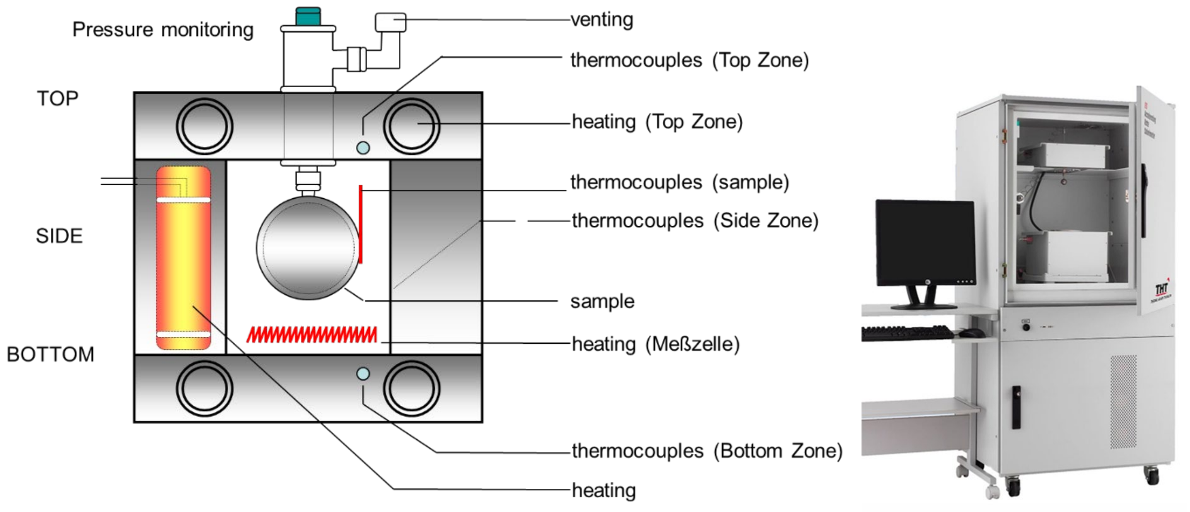


Figure 1: Schematic of an ARC an example of an ARC

The ARC was developed at Dow Chemicals in the 1970s. The adiabaticity is realized by an active control of the heat losses by adjusting the oven temperature to the temperature of a thermocouple placed at the external surface of the cell containing the sample. Thus, there is no temperature gradient between the cell and its surroundings, that is, no heat flow.
The sample is placed in a spherical cell of 10 cm^3 volume made of titanium, which may hold between 1 and 10 g. The ARC is capable of tracking directly the exothermal process under pseudoadiabatic conditions, pseudo because a part of the heat released in the sample serves to heat the cell itself (this is characterized by the thermal inertia factor: phi-factor). This phi factor is typically in the range of 1.4-3.
The cell is also linked to a pressure sensor allowing for pressure measurement.

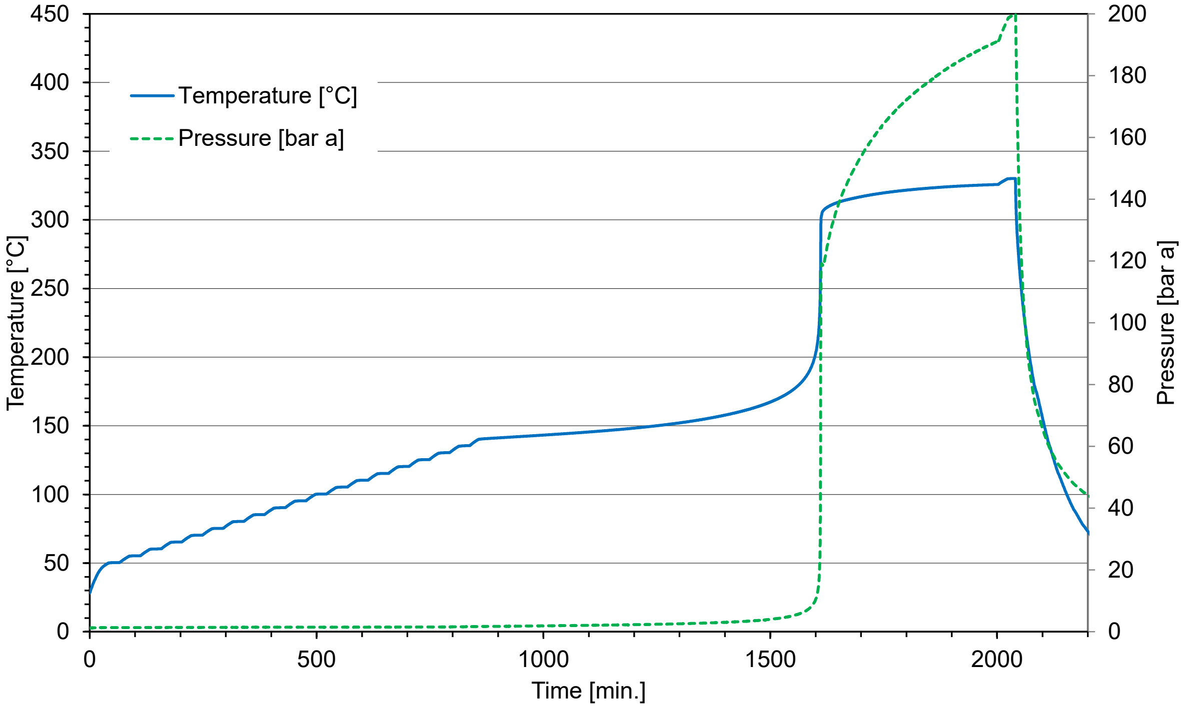
Figure 2: Typical ARC cells

This instrument can work following two different modes:

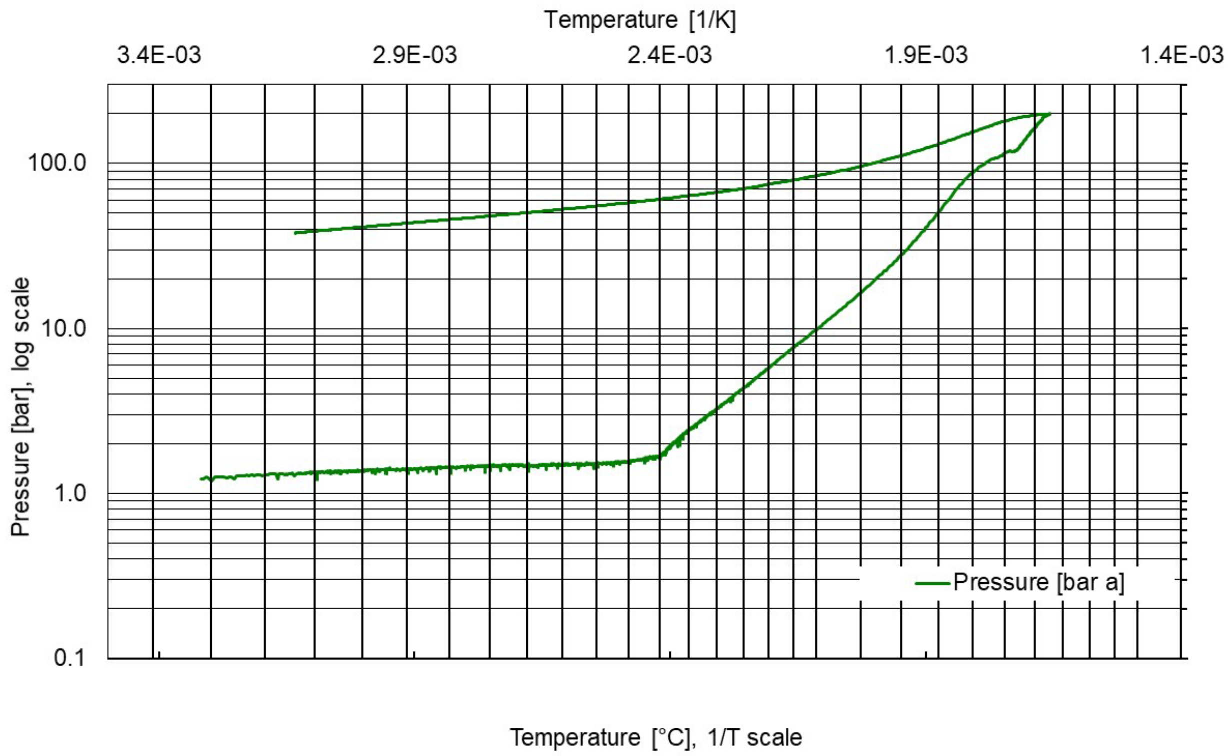
1. Heat, wait, and search (HWS): The temperature at which the exothermal reaction is detectable is searched using a defined series of temperature steps (heat). At each step, the system is stabilized for a defined time (wait); then the controller is switched to the adiabatic mode (search). If the temperature increase rate surpasses a level (typically 0.02Kmin−1), the oven temperature follows the sample temperature in the adiabatic mode (adiabatic tracking). If the temperature increase rate remains below the level, the next temperature step is achieved (heat).
2. Isothermal age mode: The sample is directly heated to the desired initial temperature. At this temperature, the instrument seeks for an exothermal effect as above.

Depending on the cell used, pressure up to 400 bar can be measured.

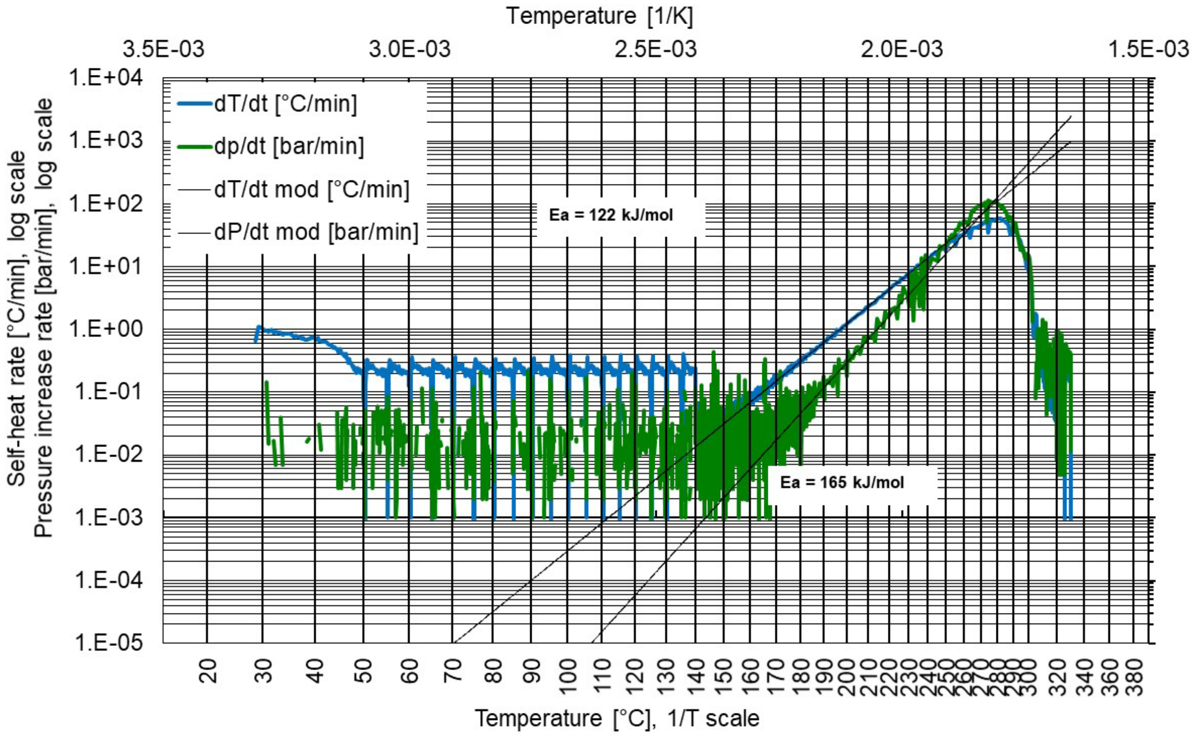
The result of an ARC measurement, after correction of the thermal inertia, is the adiabatic temperature curve: $T = f(t)$ or runaway curve. In addition, the pressure measurement delivers the pressure $P = f(t)$, which is also an indicator for the potential damage resulting from a runaway. These results are often plotted in a so-called Arrhenius diagram, with the temperature increase rate on a logarithmic scale in the ordinate as a function of the reverse temperature in Kelvin.



Temperature [°C]
Pressure [bar a]
Time [min.]



Temperature [1/K]
3.4E-03
2.9E-03
2.4E-03
1.9E-03
1.4E-03
100.0
10.0
1.0
0.1
Pressure [bar], log scale
Pressure [bar a]
Temperature [°C], 1/T scale



Temperature [1/K]
3.5E-03
3.0E-03
2.5E-03
2.0E-03
1.5E-03
1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
1.E-05
dT/dt [°C/min]
dp/dt [bar/min]
dT/dt mod [°C/min]
dP/dt mod [bar/min]
Ea = 122 kJ/mol
Ea = 165 kJ/mol
Self-heat rate [°C/min], log scale
Pressure increase rate [bar/min], log scale
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
260
270
280
290
300
320
340
360
380
Temperature [°C], 1/T scale

Calvet (C80)

(extracts from F.Stoessel, Thermal safety of chemical processes, 2nd edition, 2020, chapter 4)

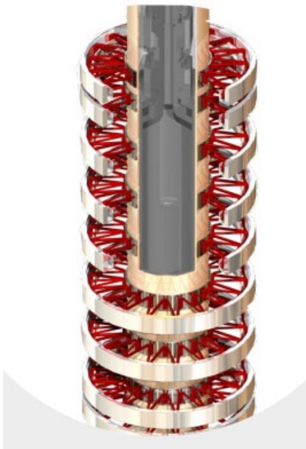


Figure 1:C80 Calorimeter . 3D sensor (picture from the Calvet Catalogue from Setaram)

It is a differential calorimeter (reference and sample) that may be operated isothermally or in the scanning mode, as a DSC, in the temperature range from room temperature to 300°C for the C80 and −196 to 275°C for the BT2.15. Compared with DSC, a dynamic experiment is longer due to the mass of the calorimeter allowing a maximum scan rate of $2 K min^{-1}$. But Calvet calorimeters show a high sensitivity of typically $0.1–1 W kg^{-1}$ (depending on the sample mass), which is essentially due to the measurement principles, based on a pile of thermocouples totally surrounding the cells (sample and reference), the so-called 3D sensor.

There is a great choice of different cells available for these calorimeters. Some of them were developed especially for safety applications.
A closed pressure tight cell is available in stainless steel, gold plated or with a glass insert. This cell, besides the thermal measurement, also allows for a measuremen tof the pressure. This gives access to the volume of gaseous (or non-condensable) product formed during the experiment.
A choice of different mixing cells is also available. As an example, a cell, especially suitable for safety studies, consists of two glass tubes arranged in such a way that the upper shorter tube fits the interior of the lower longer tube, building two separated compartments. The upper compartment can be broken by pushing a metal rod, which allows for the contents of both compartments to be mixed.
The mixing cell has many applications in process safety. For instance, it is useful to simulate an accidental intrusion of a cooling medium into a reaction mass or also for assessing the efficiency of safety measures such as quenching of reactions or dumping reaction masses. Obviously, the heat of reactions and the thermal stability of reaction masses can also be studied in these cells.

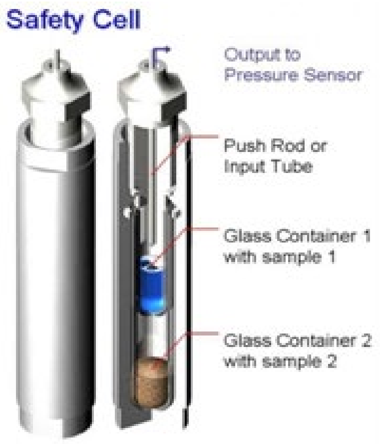
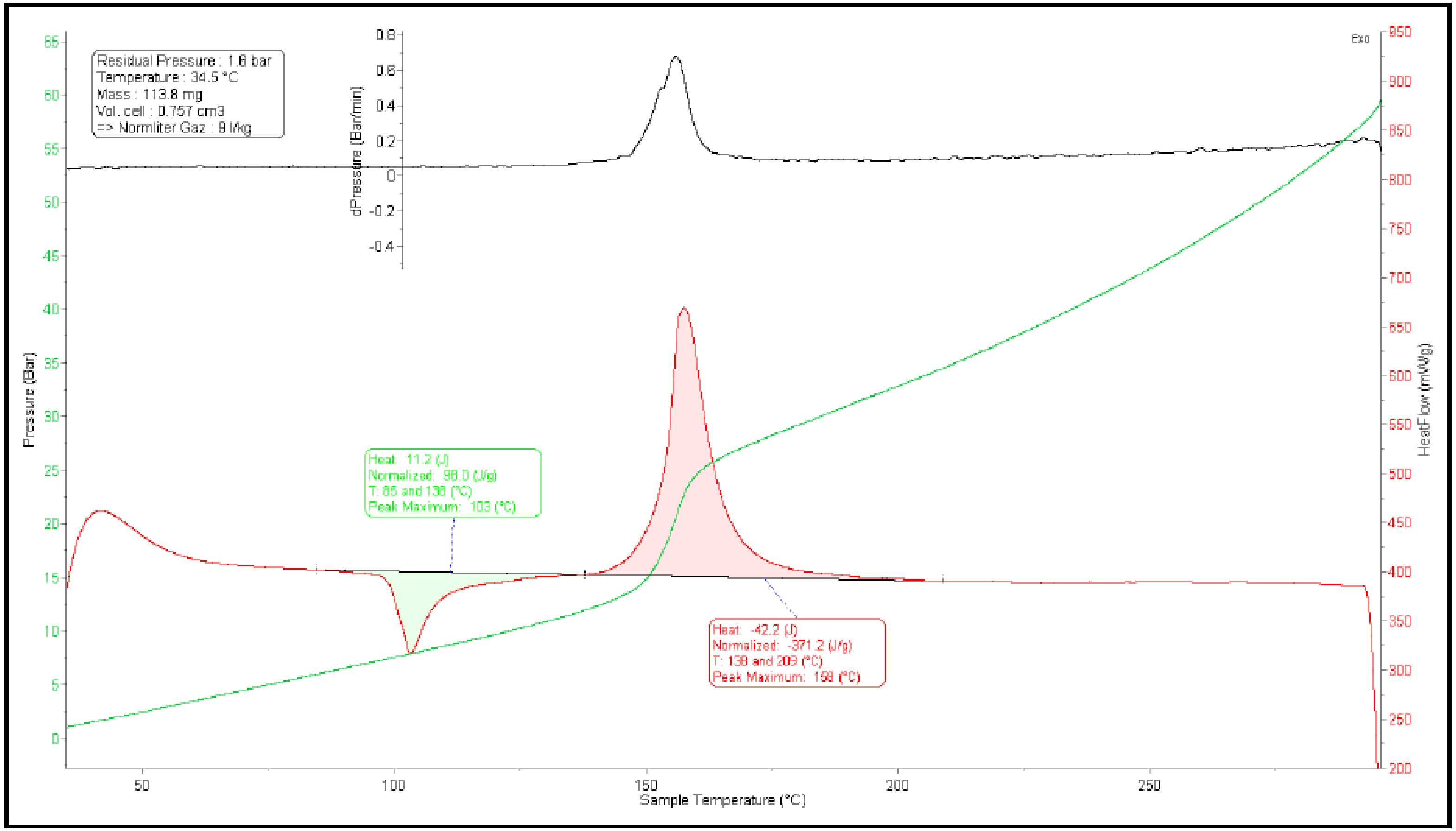


Figure 2 CG80 cells - :C80 Mixing cell

A particularly efficient experimental combination is to first perform the reaction under isothermal conditions and after the thermal signal (*q*) returned to the baseline, a temperature scan (*T*) to determine the heat of secondary reactions as well as the corresponding pressure effect. Thus, the main energetic characteristics of a reaction can be studied in one combined experiment.

The sample size is in the order of magnitude of 0.5–1.0 g. The volume of gas or non-condensable produced during the experiment can be determined from the residual pressure after the calorimeter has been cooled to 30°C. The limitation of this technique is due to the lack of agitation, which may lead to non-completed reactions.

1st endotherm	85°C - 138°C; Peak: 103°C; Q'= -98kJ/kg
1st exotherm	138°C - 209°C; Peak: 158°C; Q'= 371kJ/kg
Amount of non condensable gases	9 L/kg (@25°C, 1atm) P_end: 1.6bar (@ 34.5°C) / V_empty:0.757ml



DSC

(extracts from F.Stoessel, Thermal safety of chemical processes, 2nd edition, 2020, chapter 4)

Figure 1: DSC with DSC in measurement container

The “true” DSC uses a heating resistor placed under each crucible, controlling the crucibles’ temperature and maintaining them as equal. The difference in heating power between these heating resistors directly delivers the thermal power of the sample. Another measurement principle is the DSC, after Boersma. In this case, no compensation heating is used, and a temperature difference is allowed between sample crucible and reference crucible. This temperature difference is recorded and plotted as a function of time or temperature. The instrument must be calibrated in order to identify the relation between heat release rate and temperature difference.

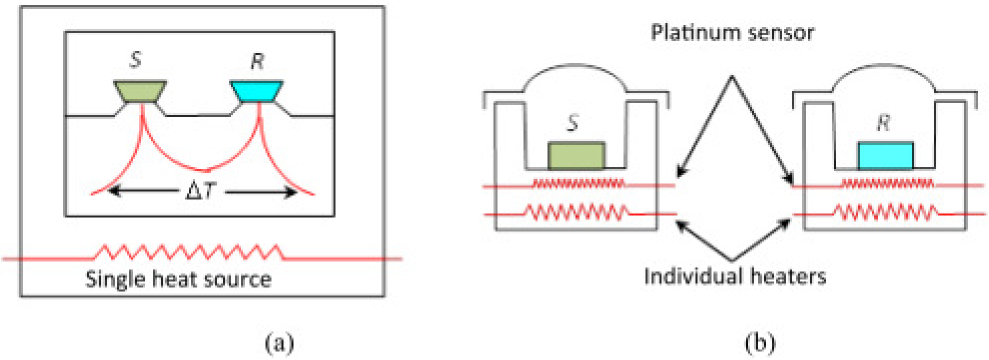


Figure 2: principle of measurement Boersma DTA and from DSC (copied from Solid-State Characterization and Techniques, D. Law and all, 2017)

The oven temperature may be controlled in two ways: the dynamic mode also called scanning mode, where the oven temperature is varied linearly with time, and the isothermal mode, where the oven temperature is maintained constant.
The DSC uses only small sample sizes in the order of some milligrams, very exothermal phenomena may be studied, even under extreme conditions, without any risk either to the laboratory personal or to the instrument. Moreover, a scanning experiment from ambient temperature to 500 ∘C with a scan rate of $4 K min^{-1}$ takes only about two hours. Thus, the DSC became a very popular instrument for screening purposes. The typical DSC sensitivity usually ranges between 2 and $20 W kg^{-1}$.

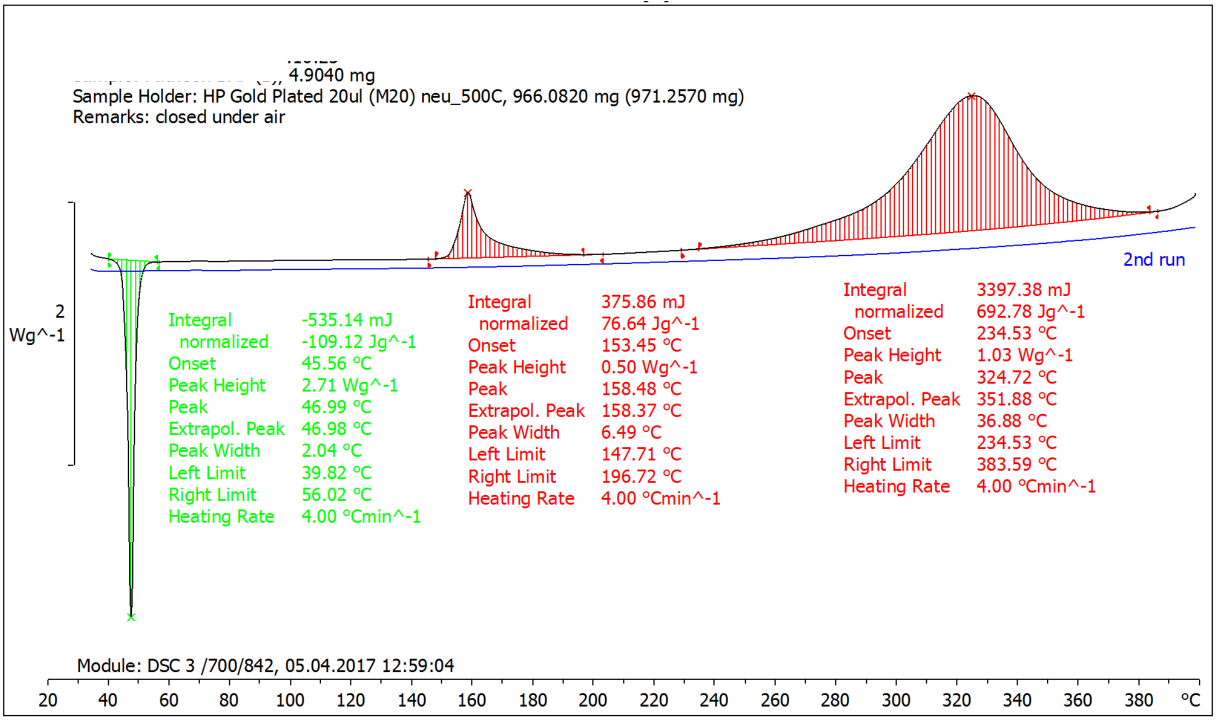
Since samples may contain some volatile compounds, during heating in scanned experiments, these compounds may evaporate, which has two consequences:

1. Evaporation is endothermal and adds a negative contribution to the heat balance, that is, to the measured signal that may mask an exothermal reaction.
2. A part of the sample is lost during the experiment, giving a false interpretation of the results.

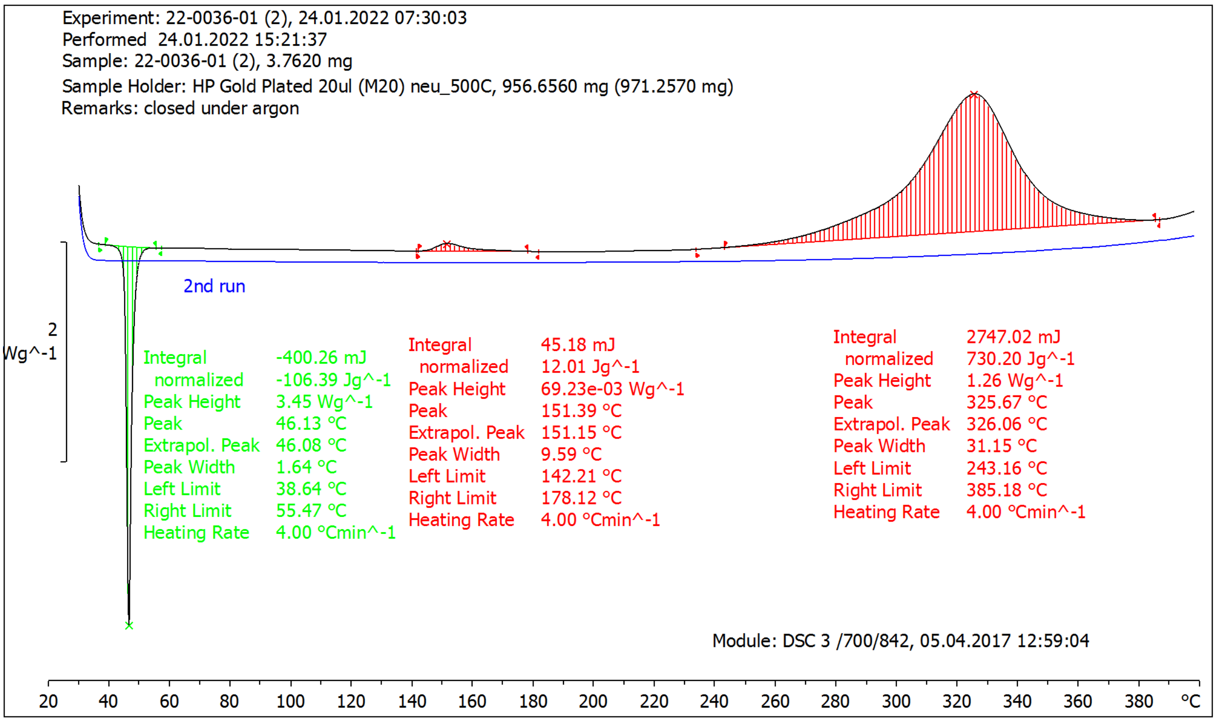
Thus, for the determination of the energy potential of a sample, it is essential to use closed pressure-resistant crucibles for these experiments. This is true for DSC but holds also for other instruments. Experience has shown that gold-plated crucibles with a volume of 50 µl and resistance to pressures up to 200 bar are best suited for safety studies.

DSC is best suited for the determination of energy potentials of secondary reactions.
Overall heat of reaction may also be determined if the reactants can be mixed at a temperature low enough to slowdown the reaction. In this case, the scan must be from low temperature too. By doing so, one must be aware that in DSC the sample cannot be stirred and there is no way of adding a reactant during reaction. Nevertheless, the dimensions of DSC crucibles allow for a short diffusion time; thus mixing is achieved by diffusion even without stirring. The aim of such scanning experiments is to simulate worst-case conditions: the sample is heated to 400 or 500°C, a temperature range where most of the organic compounds are forced to decompose. Moreover, this kind of experiment is carried out in a closed vessel, from which no decomposition product may escape, that is, under total confinement conditions. Such a thermogram shows the energetic potential of a sample as an "energy fingerprint" of the sample. Since the measurement is quantitative, the corresponding adiabatic temperature rise allows for the assessment of the severity of a runaway reaction in an easy way. This kind of screening experiment is useful for the identification of potentially hazardous mixtures.

DSC thermograms can be used to calculate the TMRad. For this purpose either more realistic estimation can be done by using a number of isothermal and/or dynamic measurements or by using important safety margins to ensure a conservative estimate and single measurements (will be further discussed in the thermal stability lecture).



4.9040 mg
Sample Holder: HP Gold Plated 20ul (M20) neu_500C, 966.0820 mg (971.2570 mg)
Remarks: closed under air
2nd run
2
Wg^-1
Integral -535.14 mJ
normalized -109.12 Jg^-1
Onset 45.56 °C
Peak Height 2.71 Wg^-1
Peak 46.99 °C
Extrapol. Peak 46.98 °C
Peak Width 2.04 °C
Left Limit 39.82 °C
Right Limit 56.02 °C
Heating Rate 4.00 °Cmin^-1
Integral 375.86 mJ
normalized 76.64 Jg^-1
Onset 153.45 °C
Peak Height 0.50 Wg^-1
Peak 158.48 °C
Extrapol. Peak 158.37 °C
Peak Width 6.49 °C
Left Limit 147.71 °C
Right Limit 196.72 °C
Heating Rate 4.00 °Cmin^-1
Integral 3397.38 mJ
normalized 692.78 Jg^-1
Onset 234.53 °C
Peak Height 1.03 Wg^-1
Peak 324.72 °C
Extrapol. Peak 351.88 °C
Peak Width 36.88 °C
Left Limit 234.53 °C
Right Limit 383.59 °C
Heating Rate 4.00 °Cmin^-1
Module: DSC 3 /700/842, 05.04.2017 12:59:04
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 °C



Experiment: 22-0036-01 (2), 24.01.2022 07:30:03
Performed 24.01.2022 15:21:37
Sample: 22-0036-01 (2), 3.7620 mg
Sample Holder: HP Gold Plated 20ul (M20) neu_500C, 956.6560 mg (971.2570 mg)
Remarks: closed under argon
2nd run
2
Wg^-1
Integral -400.26 mJ
normalized -106.39 Jg^-1
Peak Height 3.45 Wg^-1
Peak 46.13 °C
Extrapol. Peak 46.08 °C
Peak Width 1.64 °C
Left Limit 38.64 °C
Right Limit 55.47 °C
Heating Rate 4.00 °Cmin^-1
Integral 45.18 mJ
normalized 12.01 Jg^-1
Peak Height 69.23e-03 Wg^-1
Peak 151.39 °C
Extrapol. Peak 151.15 °C
Peak Width 9.59 °C
Left Limit 142.21 °C
Right Limit 178.12 °C
Heating Rate 4.00 °Cmin^-1
Integral 2747.02 mJ
normalized 730.20 Jg^-1
Peak Height 1.26 Wg^-1
Peak 325.67 °C
Extrapol. Peak 326.06 °C
Peak Width 31.15 °C
Left Limit 243.16 °C
Right Limit 385.18 °C
Heating Rate 4.00 °Cmin^-1
Module: DSC 3 /700/842, 05.04.2017 12:59:04
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 °C

Reaction calorimetry

(extracts from F.Stoessel, Thermal safety of chemical processes, 2nd edition, 2020, chapter 4)

Basically, reaction calorimeters are designed in such a way that they perform a reaction under conditions that are as close as possible to plant operation conditions. This means that the temperature of a reaction calorimeter may be controlled in the isothermal mode or in a temperature-programmed mode. Thus the “cell” of reaction calorimeters is a stirred tank reactor.

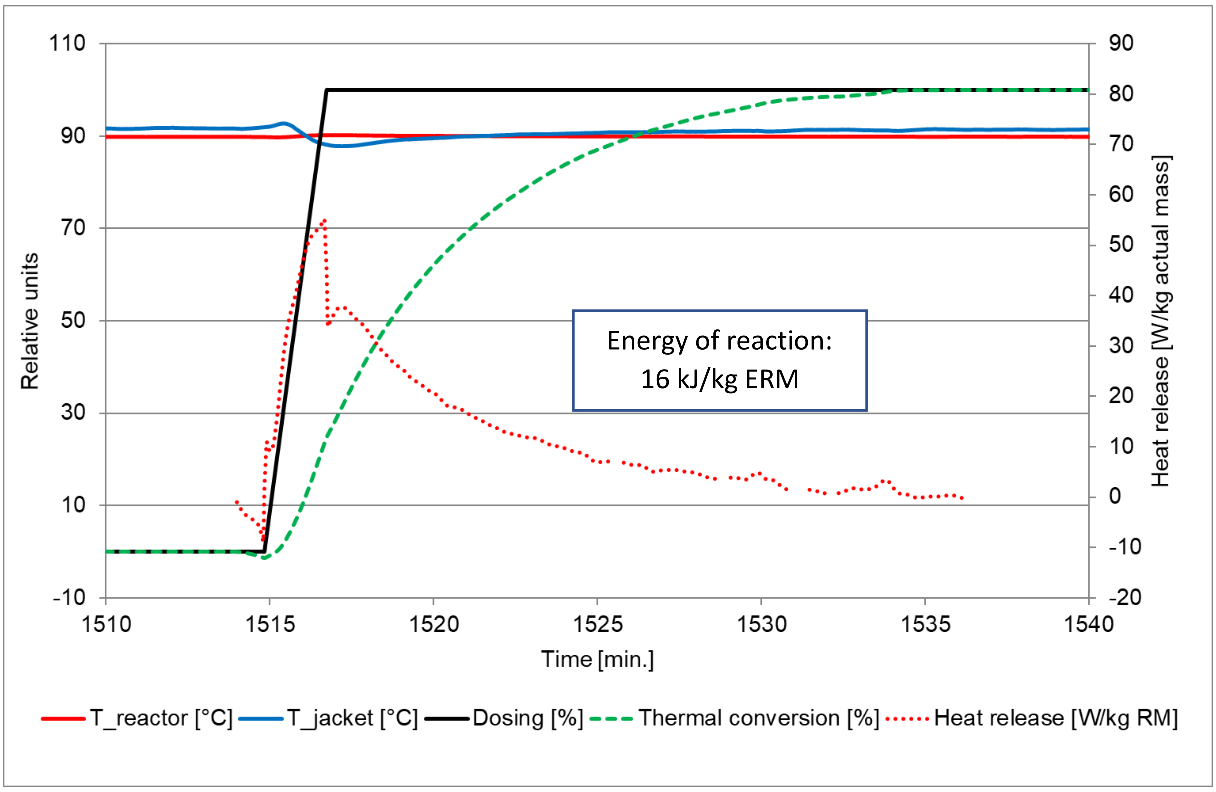
There are different types of calorimeters, the main measurement principles are:

- Heat flow calorimeters (the totality of the heat produced in the reactor is exchanged with the jacket). A fast In order to realize this condition, a fast circulation of the heat carrier in the jacket allows for a nearby constant temperature in the jacket, so the heat flow can be measured based on the temperature difference between the jacket and the reaction mass:
  $q_{ex} = U \cdot A \cdot (T_r - T_c) = q_{rx}$
  UA is determined by calibration
- Heat balance calorimeters: a balance on the temperature increase of the heat carrier is measured. In order to get a measurable temperature difference between inlet and outlet, the mass flow rate must be reduced. Therefore, in these instruments the temperature control is less precise.
  $q = \dot{m} \cdot c'_p \cdot \left(T_{c,out} - T_{c,in}\right)$
- Compensation calorimeters: Calorimeters working following the compensation principle use an electrical heater with a power at least equal to the maximum power of the reaction or phenomenon to be measured. This heater is switched on before starting the reaction, and the reactor is cooled by a heat carrier flowing in a jacket. When an exothermal phenomenon takes place, the temperature controller reduces the power of the heater in order to maintain the temperature at the desired set point. Of course when an endothermal phenomenon takes place, the power of the heater is increased. In this way the measured power of the heater is a mirror image of the power released in the calorimeter.

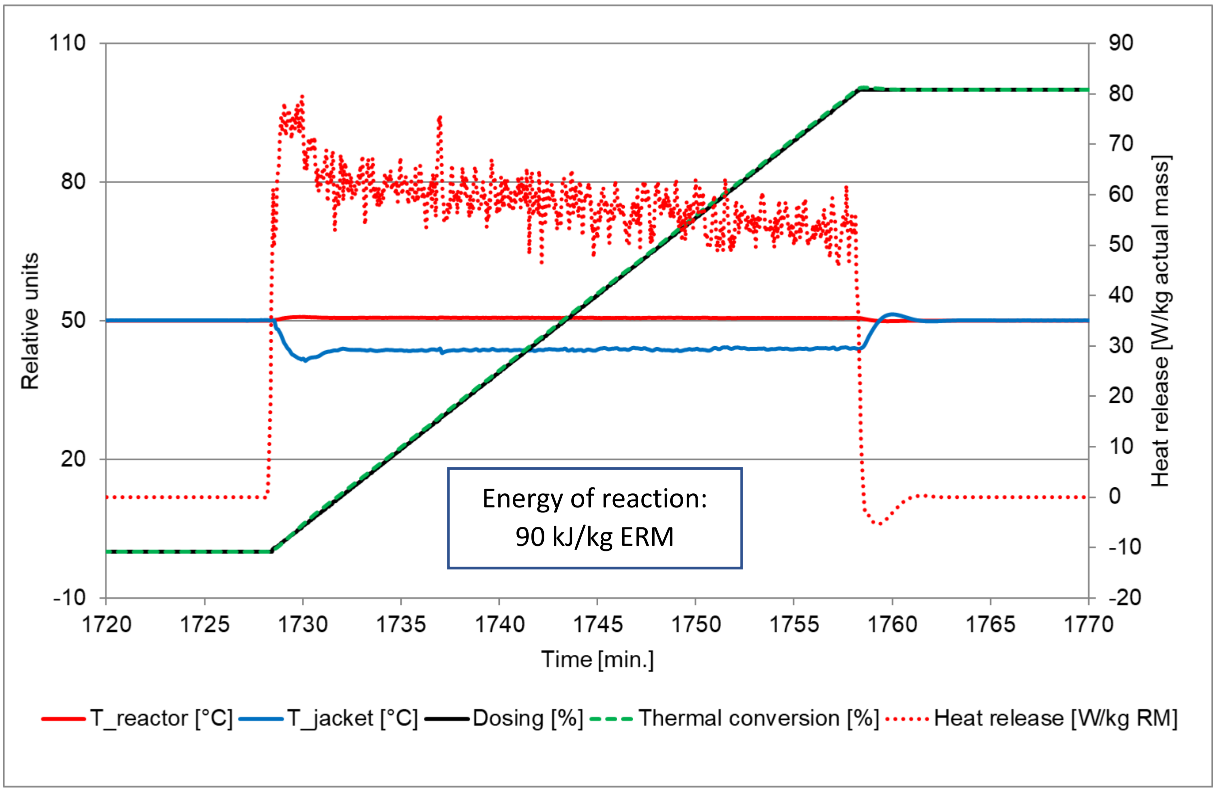
A reaction calorimeter must allow addition of reactants in a controlled way, distillation, or refluxing and reactions with gas release. In summary, they must perform the same operations as an industrial stirred tank reactor, with a major difference: they allow tracking the thermal phenomena occurring during these operations.

The reaction calorimeters were initially developed for safety analysis but very soon their benefits for process development and scale-up were recognized].

Reaction calorimetry was applied to a great diversity of different reactions, including polymerization, Grignard reactions, nitrations, hydrogenations, epoxydations and more.



110
90
70
50
30
10
-10
Relative units
90
80
70
60
50
40
30
20
10
0
-10
-20
Heat release [W/kg actual mass]
1510
1515
1520
1525
1530
1535
1540
Time [min.]
Energy of reaction:
16 kJ/kg ERM
T_reactor [°C]
T_jacket [°C]
Dosing [%]
Thermal conversion [%]
Heat release [W/kg RM]



110
80
50
20
-10
Relative units
90
80
70
60
50
40
30
20
10
0
-10
-20
Heat release [W/kg actual mass]
1720
1725
1730
1735
1740
1745
1750
1755
1760
1765
1770
Time [min.]
Energy of reaction:
90 kJ/kg ERM
T_reactor [°C]
T_jacket [°C]
Dosing [%]
Thermal conversion [%]
Heat release [W/kg RM]

TAM (Thermal activity monitor)

(extracts from F.Stoessel, Thermal safety of chemical processes, 2nd edition, 2020, chapter 4)

Figure 1: TAM equipments (right picture taken from https://www.tainstruments.com/tam-iv/)

It is a differential isothermal calorimeter with a high sensitivity, able of measuring in the order of magnitude of μ W. With a sample size of 1g, this corresponds to 1mWkg^{-1}.This sensitivity is achieved by a battery of thermocouples surrounding the sample and by a high precision thermostat controlling the temperature with an accuracy of 0.1mK.

This instrument is well suited for the study of long-term stability at storage (isothermal conditions). For example, decomposition with energy of 500 kJ kg^{-1}, and with a heat release rate of 3mWkg^{-1}, would reach a conversion of 1.5% in one month. This is a typical heat release rate that can be measured by this instrument. Thus, it finds its applications in the field of process safety for the study of heat accumulation problems.

Sometimes it is also used to confirm extrapolation of the heat release rate measured by isothermal experiments in DSC. This technique allows for the study of a reaction over a large temperature range (ΔT: 65–200°C) and over 5 orders of magnitude for the thermal power (from 0.02 to over 200Wkg^{-1}).

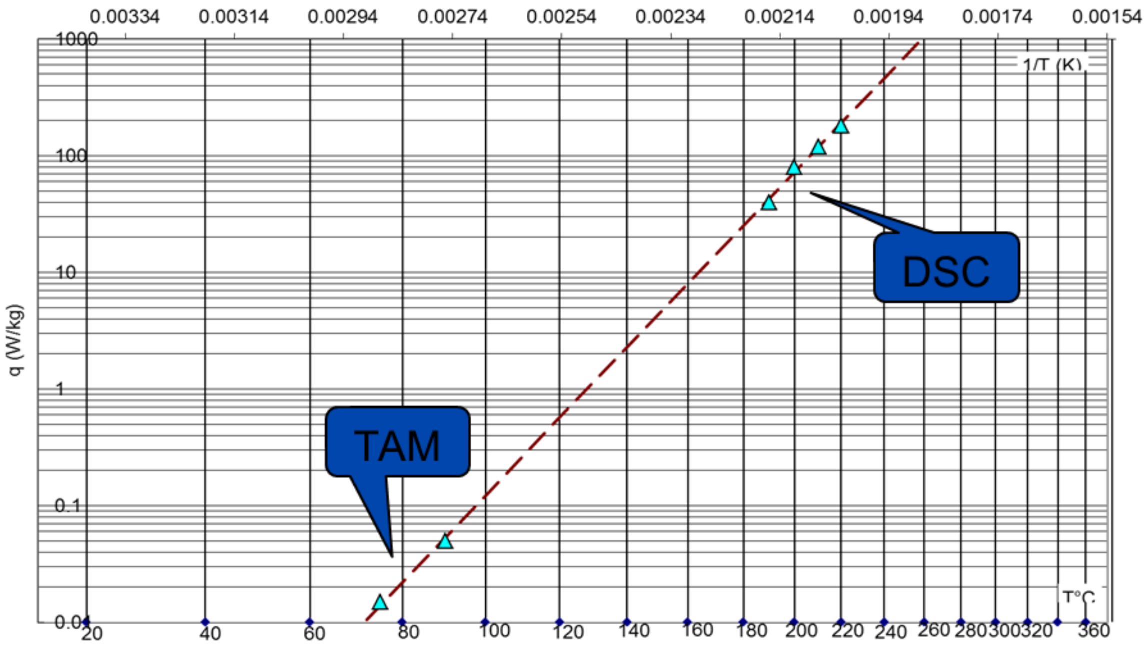
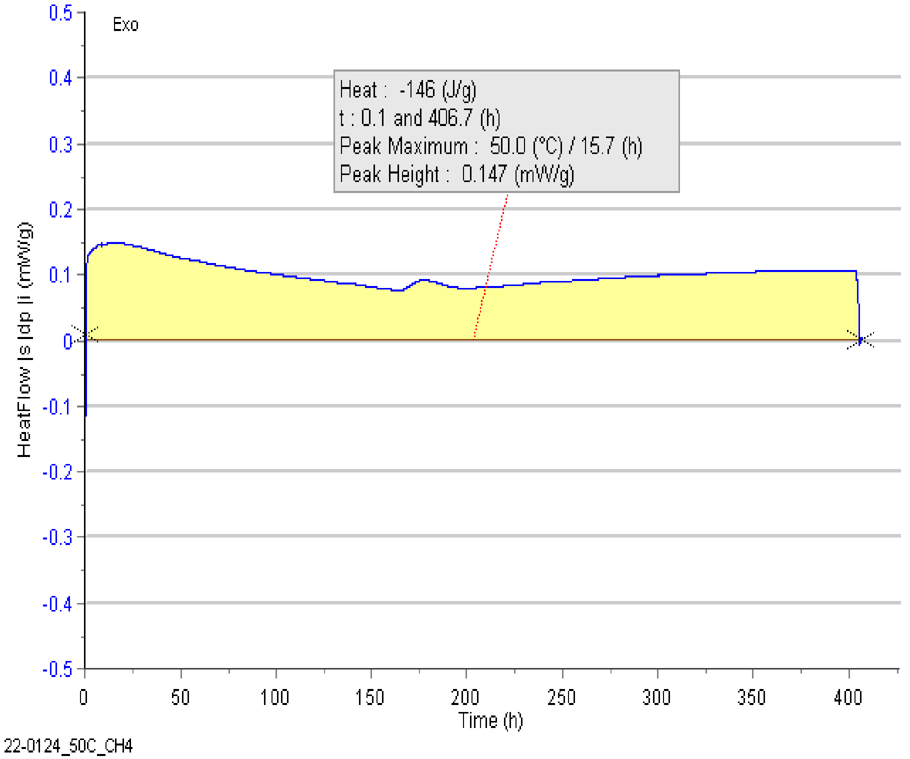
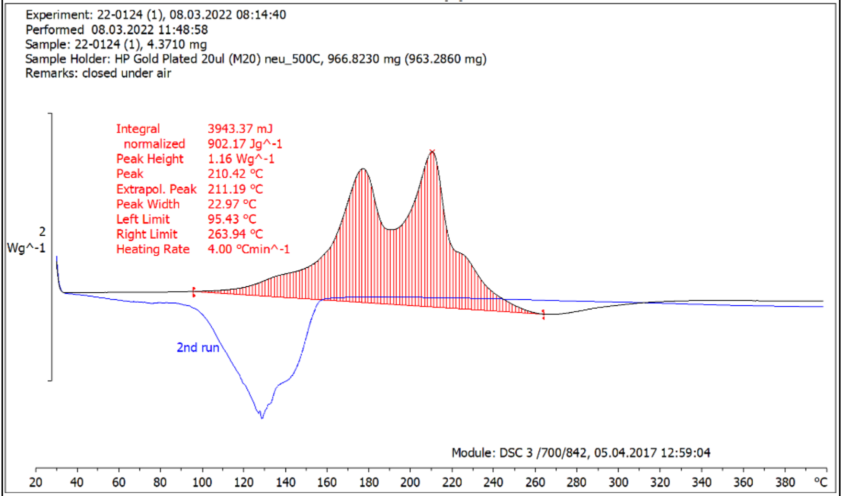


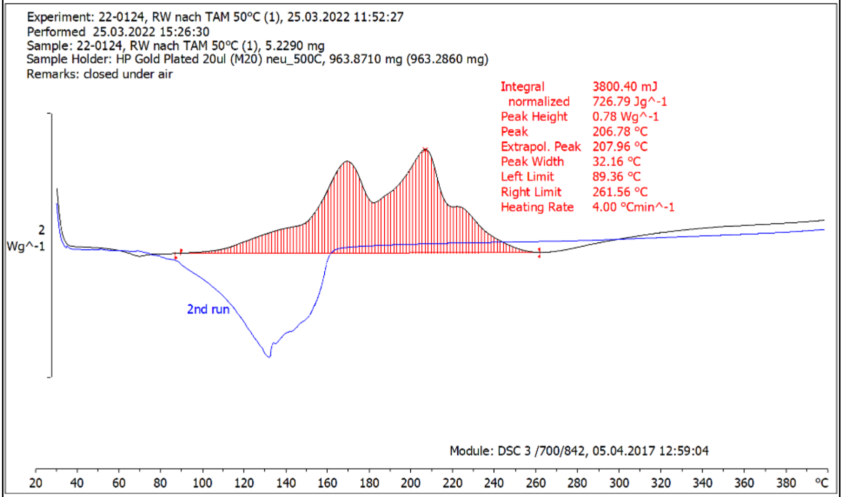
Figure 2: Confirmation of extrapolation made with DSC



Exo
Heat : -146 (J/g)
t : 0.1 and 406.7 (h)
Peak Maximum : 50.0 (°C) / 15.7 (h)
Peak Height : 0.147 (mW/g)
HeatFlow |s |dp |i (mW/g)
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
0
50
100
150
200
250
300
350
400
Time (h)
22-0124_50C_CH4



Experiment: 22-0124 (1), 08.03.2022 08:14:40
Performed 08.03.2022 11:48:58
Sample: 22-0124 (1), 4.3710 mg
Sample Holder: HP Gold Plated 20ul (M20) neu_500C, 966.8230 mg (963.2860 mg)
Remarks: closed under air
Integral 3943.37 mJ
normalized 902.17 Jg^-1
Peak Height 1.16 Wg^-1
Peak 210.42 °C
Extrapol. Peak 211.19 °C
Peak Width 22.97 °C
Left Limit 95.43 °C
Right Limit 263.94 °C
Heating Rate 4.00 °Cmin^-1
2
Wg^-1
2nd run
Module: DSC 3 /700/842, 05.04.2017 12:59:04
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 °C



Experiment: 22-0124, RW nach TAM 50°C (1), 25.03.2022 11:52:27
Performed 25.03.2022 15:26:30
Sample: 22-0124, RW nach TAM 50°C (1), 5.2290 mg
Sample Holder: HP Gold Plated 20ul (M20) neu_500C, 963.8710 mg (963.2860 mg)
Remarks: closed under air
Integral 3800.40 mJ
normalized 726.79 Jg^-1
Peak Height 0.78 Wg^-1
Peak 206.78 °C
Extrapol. Peak 207.96 °C
Peak Width 32.16 °C
Left Limit 89.36 °C
Right Limit 261.56 °C
Heating Rate 4.00 °Cmin^-1
2
Wg^-1
2nd run
Module: DSC 3 /700/842, 05.04.2017 12:59:04
20 40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 °C

VSP (Vent size package)

(extracts from F.Stoessel, Thermal safety of chemical processes, 2nd edition, 2020, chapter 4)

The VSP calorimeter was developed with the aim of providing data for pressure relief design. The working principle is similar to the ARC, but it is a low-phi calorimeter (usually 1.05 to 1.15). It requires less intensive correction than the ARC.

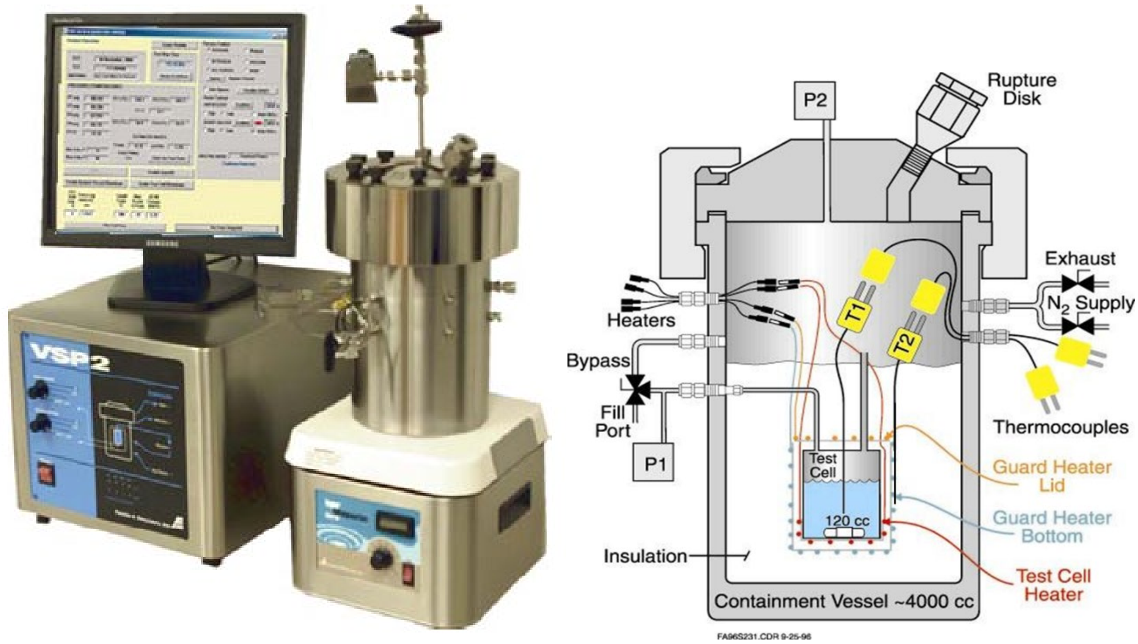


Figure 1: VSP2 and schematic of the VSP2 (Fauske and Associates LLC)

The adiabaticity is realized by thermal insulation, but by an active control of the heat losses by adjusting the oven temperature to the temperature of a thermocouple placed at the external surface of the cell containing the sample. Thus, there is no temperature gradient between the cell and its surroundings, that is, no heat flow. The sample is placed in a thin-walled cylindrical cell of 110 cm3 volume. It holds typically 60-70 ml of sample. This thin-walled metal cell has the drawback of a poor pressure resistance. This is compensated for by placing the test cell in an autoclave equipped with a pressure controller, maintaining the pressure difference between the test cell contents and the autoclave below a predefined value by controlling the pressure in the autoclave with nitrogen injections. So there are two tracking devices.

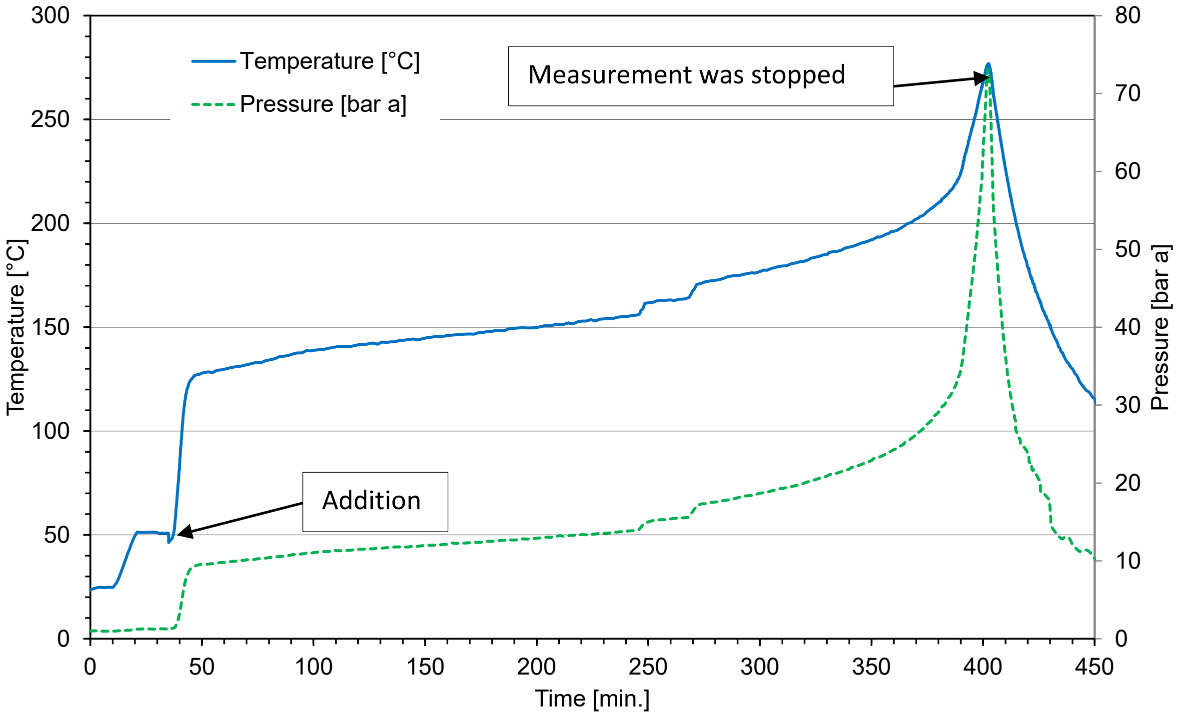
In the cell a magnetic agitator is present. The test cell and test method are highly customizable. The test cell can be constructed stainless steel or Hastelloy C and can also be glass lined. Glass-lined test cells result in an increase of the Φ-factor. Test cell designs can include wall baffles, dip tubes, multiple thermocouples, scaled vents, and other features to help simulate a process upset.
The autoclave not only may be closed for standard experiments but also may be opened by a valve, allowing for pressure relief simulation and determination of foaming (flow regime) properties or the determination of the amount of liquid, vapor, or gas discharged.This calorimeter is basically a small chemical reactor but is specially designed to provide directly scalable calorimetric data in the context of vent sizing and emergency relief system design.

Figure 2: VSP cell and cell with heater

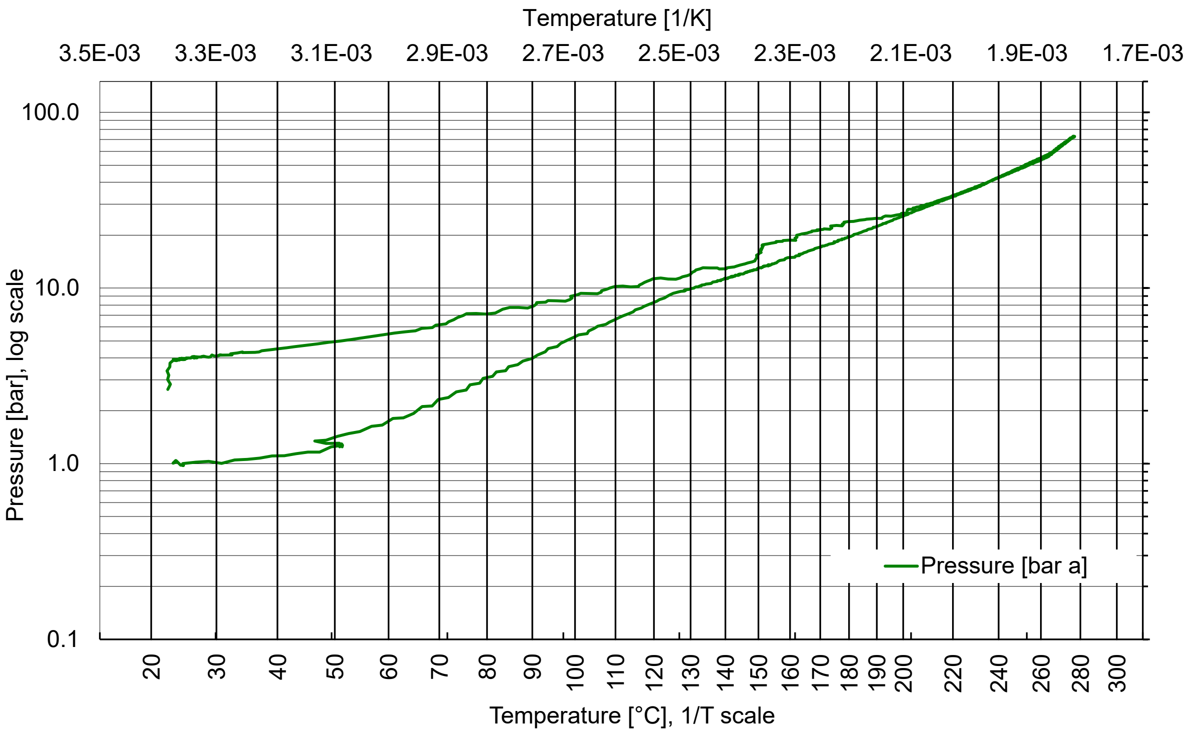
This instrument can work following two different modes:

1. Heat, wait, and search (HWS): The temperature at which the exothermal reaction is detectable is searched using a defined series of temperature steps (heat). At each step, the system is stabilized for a defined time (wait); then the controller is switched to the adiabatic mode (search). If the temperature increase rate surpasses a level (typically $0.02 K min^{-1}$), the oven temperature follows the sample temperature in the adiabatic mode (adiabatic tracking). If the temperature increase rate remains below the level, the next temperature step is achieved (heat).
2. Isothermal age mode: The sample is directly heated to the desired initial temperature. At this temperature, the instrument seeks for an exothermal effect as above.

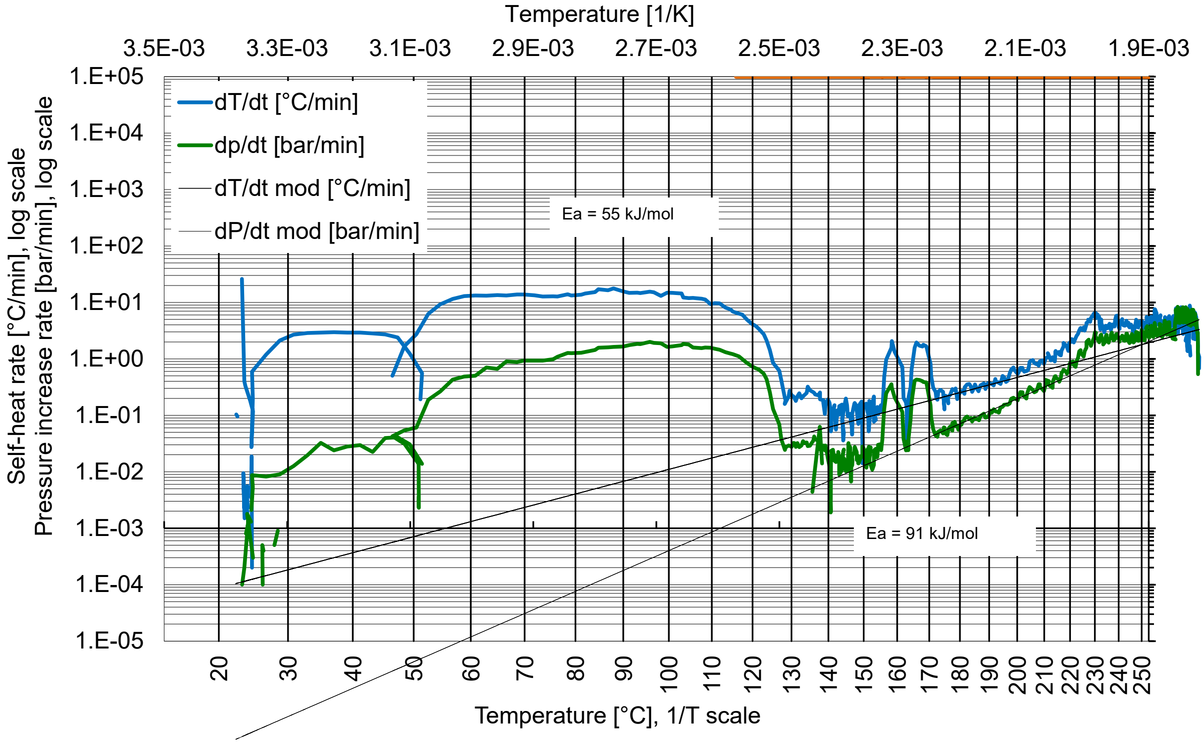
The maximum pressure is 110 bar, but experiments are usually stopped when ca 80 bar are reached. The result of a VSP measurement, after correction of the thermal inertia, is the adiabatic temperature curve: $T = f(t)$ or runaway curve. In addition, the pressure measurement delivers the pressure $P = f(t)$, which is also an indicator for the potential damage resulting from a runaway. These results are often plotted in a so-called Arrhenius diagram, with the temperature increase rate on a logarithmic scale in the ordinate as a function of the reverse temperature in Kelvin.



Temperature [°C]
Pressure [bar a]
Measurement was stopped
Addition
Time [min.]
300
250
200
150
100
50
0
80
70
60
50
40
30
20
10
0
0
50
100
150
200
250
300
350
400
450



Temperature [1/K]
3.5E-03
3.3E-03
3.1E-03
2.9E-03
2.7E-03
2.5E-03
2.3E-03
2.1E-03
1.9E-03
1.7E-03
100.0
10.0
1.0
0.1
Pressure [bar], log scale
Pressure [bar a]
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
220
240
260
280
300
Temperature [°C], 1/T scale



Temperature [1/K]
3.5E-03
3.3E-03
3.1E-03
2.9E-03
2.7E-03
2.5E-03
2.3E-03
2.1E-03
1.9E-03
1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
1.E-05
dT/dt [°C/min]
dp/dt [bar/min]
dT/dt mod [°C/min]
dP/dt mod [bar/min]
Ea = 55 kJ/mol
Ea = 91 kJ/mol
Self-heat rate [°C/min], log scale
Pressure increase rate [bar/min], log scale
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
250
Temperature [°C], 1/T scale