CALORIMETER C 80

Mixing and reaction calorimeter

SETARAM
Groupe sfim

C 80...the vital complement to DSC

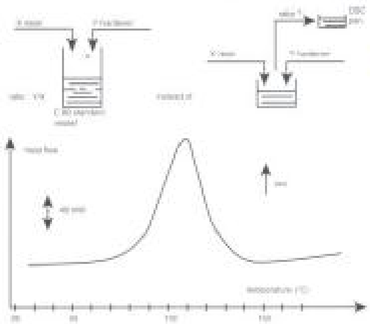
Calorimetry is well-known measuring method which has long been in use.
Over the last few years it has greatly advanced through automation and digitalised equipment. However, this development in calorimeters has been partly over shadowed by the rapid growth in thermal analyzers of the DSC type.
Although the DSC method has provided thermal analysis techniques applicable to industrial laboratories, it does not solve all the problems of analysis. With its restriction to the study of small-scale samples and its inability to let two liquid or solid products mix, the DSC method does not cover a wide ranging field of applications open to calorimetry.
SETARAM has available a purpose-built calorimeter for handling these operations :
this is the **C 80** calorimeter, which is sturdy, easy to use, able to scan from ambient temperature to 300°C and digitized.
With all these features the **C 80** calorimeter is the appropriate and vital complement to the DSC analyzer.

C 80... which measurement ?

When material is heated or cooled, its structure and chemical composition undergo changes. These transformations are associated with heat exchange.
When two solid or liquid materials are brought together at a given temperature they can react or mix with each other... These reactions or mixtures are also associated with heat exchange.
The calorimetric method used to measure this heat flow which provides numerous pieces of information on the behaviour and the thermal properties of the material (fusion, polymerization, decomposition, oxidation, heat capacity...) or the materials brought together (reaction, dilution, hydration, wetting...).
The calorimetric measurement provides the value of the transformation heat or that from the reaction, as well as showing the temperature of the thermal phenomenon (in scanning mode).

C 80... an entirely automated calorimeter

The **C 80** calorimeter comes in a new and entirely automated format. For even greater ease of operation and flexibility of use the **C 80** is entirely controlled by the computer via the CS 32 controller (32-bit microprocessor).
Programming and controlling the temperature of the furnace surrounding the calorimetric transducers, acquiring and digitizing the temperature and heat-flow signals from the transducers, printing the signals... all these operations are entirely automated with the SETSOFT new software packages for use with WINDOWS™.
With the CS 32 controller the **C 80** becomes a calorimeter with greater efficiency and higher performance to help research and quality control laboratories.

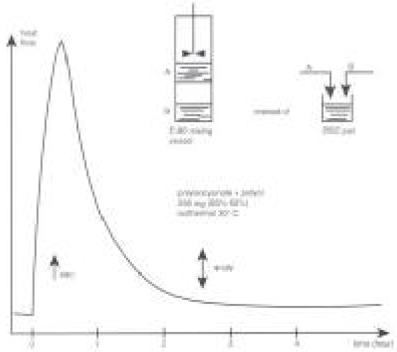


C 80... the complement to DSC

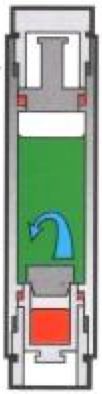
Two examples of different applications are enough to show how the DSC and the calorimetric methods complement each other : condensation of an epoxy resin and polymerization of polyurethane.
1- Epoxy resin condenses when it meets a small quantity of hardener. So, when working with a tenth of a milligramme of resin introduced into a DSC crucible, how is the required amount of hardener to be accurately added when it represents a mass generally less than a milligramme ? There is an obvious problem in knowing the ratio of resin to hardener. By using the large volume vessel on the **C 80** (15 cm³) the analysis is carried out on a greater mass of resin (a few grammes) and the ratio of resin to hardener is accurately determined.

2- Polyurethane is produced by the reaction between poly-isocyanate and polyol.
As soon as both liquids mix the reaction starts at ambient temperature.
In DSC both components have to be brought together in the same crucible before the test starts. With the **C 80** both liquids are isolated in a mixing vessel, then brought together at the required moment. There are obvious advantages to the calorimetric method : clearly defined start to the reaction (t=0) and full and accurate measurement of the heat of polymerization.

If you already use the DSC method ?
Then the **C 80** calorimeter is of interest for simulating your reactions and thermal transformations on larger-volume samples, as well as simulating your mixing reactions.



C 80... research and control



C 80... the mixing and reaction calorimeter

The **C 80** calorimeter can be used much as a DSC analyzer in temperature scanning, but with large-volume samples. However it has the unique capability of being able to be used as a mixing and reaction calorimeter.
Mounted on an reversal fitting and with the use of mixing vessels, it is the ideal tool for simulating mixing operations, which are regularly found in industrial processes from synthesis to the production stage : operations involving diluting, neutralizing, wetting, reacting...
The information gathered from the calorimetric test is used for setting the reactor cooling conditions, the dissolution rate for a substance, the selection of a solvent, the stability of a compound... all of which is useful for carrying out an industrial reaction correctly.

C 80... an impressive range of vessels

Research and quality control laboratories often have different aims, but their needs for measuring thermodynamic values as well as simulating thermal procedures are sometimes the same.
With very wide range of experimental vessels the **C 80** calorimeter provides everyone with unlimited measuring and simulating facilities :

- mixing and reaction vessel
- liquid or gas circulation vessel
- liquid percolation vessel
- pressure transducer vessel
- vessels for determining heat capacity, thermal conductivity, heat of vaporization...

Liquid, solid or gas : any material can be analyzed with the **C 80** calorimeter.
All that is needed is to select the experimental vessel appropriate for the measurement.
A corrosive environment ?
There are vessels available made of stainless steel or Hastelloy C.

C 80... the computer-controlled calorimeter

The use of the new controller and SETSOFT have greatly improved the technical features of the **C 80** : greater flexibility of use, faster acquisition and better exploitation of the signal.
Instrument control is via the computer's keyboard, working through an operating software package which is based on pre-programmable procedures.
SETSOFT's multi-module operation also provides for multi-tasking operation : the computer can be used simultaneously for piloting a thermal analysis system and for carrying out any other task (for instance data processing).
Numerous facilities for the signal display on the screen are available : modifying the scales, the colors, the textual commentaries,...
Numerous facilities are also available for treating curve using the base software packages as well as using different optional software packages (heat capacity, kinetic data...).
Several curves can be superimposed for comparison (refer also to SETSOFT brochure).

C 80... varied measurements and applications

The **C 80** calorimeter is aimed at research and quality control laboratories involved with simulating industrial processes, measuring thermodynamic values, studying mixtures in fields as varied as industrial chemistry, petrochemical, pharmaceutical or food industries, as well as those dealing with explosives, nuclear engineering, batteries, together with the cement and plaster industries,...
Among the measurements and applications currently carried out with the **C 80** calorimeter are :

- transformations within materials (fusion, dehydration, transition) so as to study the thermal balance of the operation
- decomposition of organic products and measurement of the pressure
- simulation of reaction under pressure
- dilution, neutralization, wetting, hydration
- liquid-liquid, liquid-solid reactions
- liquid adsorption on porous materials
- gas adsorption on catalysts, zeolites
- measurements of heat capacity, thermal conductivity, heat of vaporization, vapour pressure

... and many other applications or measurements which the **C 80** calorimeter will enable you to develop and refine.

C 80... a sturdy and flexible calorimeter

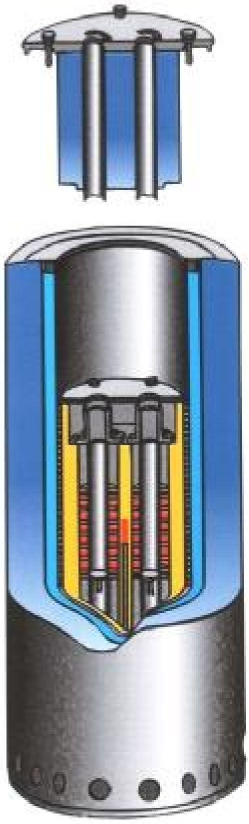
Depending on the application the **C 80** calorimeter can be used with or without the reversal fitting, giving identical performances. A very wide range of experimental vessels is available for both versions of the **C 80** so as to comply with your measurement and application requirements.

C 80... a heat-flux calorimeter

The **C 80** calorimeter is a modern version of calorimeters designed on the Calvet principle and used at either constant or variable temperature between ambient temperature and 300°C.
The **C 80** is made up of a conducting calorimetric block surrounding the heat transducers. This block is itself surrounded by the heating element and arranged in an insulated chamber.
The sample contained in an experimental vessel is introduced into the hole and rests in a sensing space, entirely surrounded by the heat transducers.
An identical vessel without a sample is arranged in the second hole.
The differential arrangement of the heat transducers provides a signal proportional to the heat exchanged by the sample as a result of cancelling out of the interference connected with temperature control of the calorimetric block.

The **C 80** can be set for temperature scanning at low scanning rates (limit : 2°C.min^{-1}).
Forced ventilation provides a rapid return to ambient temperature. For work involving mixing and reaction the **C 80** is mounted on an reversal mechanism, which is driven by an electric motor.
There are mixing vessels made especially for this fitting.

The calorimeter can be calibrated very accurately at any temperature using a resistance vessel which simulates the experimental vessel and which delivers a calibrated electrical power (Joule effect method).



C 80... an accessible calorimeter

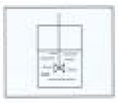
The **C 80** calorimeter is sealed by a removable cap providing the instrument with good insulation. Removing the cap enables the cap hole to be used as an access chamber for the calorimeter's working area. The chamber provides the internal fixings for the mixing vessels and the arrangements for temperature pre-stabilisation features for fluid samples before introduction.
This accessibility to the **C 80** enables numerous experimental set-ups to be produced where a connection to the outside is needed :

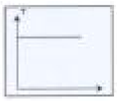
- mechanical connections (membrane perforation, agitation...)
- electrical connections (Joule effect, calibration...)
- fluid connections (vacuum application, gas or liquid circulation, pressurization, percolation...)

C 80... manifold operations

Operating the **C 80** calorimeter, with or without inversion, at constant or variable temperature, and with vessels which are either sealed or connected to the outside, provides a wide-range and ever-expanding field of experiments.

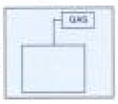
Mixing reaction
Simulating mixing and reaction by reversing the calorimeter or mechanical agitation.

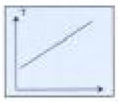




Constant temperature
Very common operating mode for the **C 80** when studying mixtures and reactions.

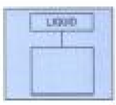
Gas-pressure interaction
Inert gas circulation (sample protection) or active gas circulation (oxidation, reduction). Gas adsorption under variable pressure. Reaction under gas pressure. Measurement for the pressure of decomposition.





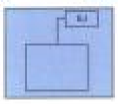
Variable temperature
Rising and falling temperature scanning for studying transformations and transitions.

Liquid circulation
Liquid percolation (adsorption). Liquids mixing in the "flow" mode.



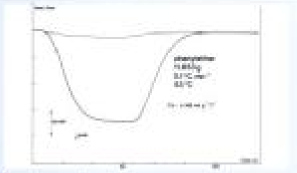
Step-rising temperature
Temperature scanning by step rise for measuring heat capacity.

Electrical connections
Electrical calibration by Joule effect. Experimental set-up for measuring thermal conductivity.



C 80...
varied measurements

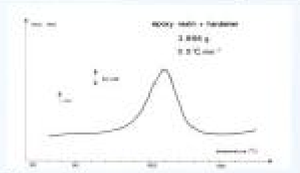
Very varied measurements can be undertaken with the **C 80** bearing in mind the numerous experiment facilities offered by the calorimeter and the different experimental vessels. Let us look a few examples.



Heat capacity

The **C 80** calorimeter is fully designed for measuring the heat capacity of solids and liquids by either the continuous or step temperature scanning method.

In either case the heat capacity is determined by the difference between two successive tests without a sample (blank run) and with a sample (e.g. : Cp of phenyl ether at 53°C by the step method).

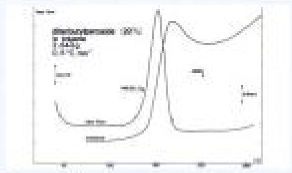


Polymerization

By using the volume contained in the **C 80**'s experimental vessel (15 cm^3), simulating the reaction produced by polymerization or curing is carried out on a considerable mass of resin (several grammes).

To establish the hardener to resin ratio accurately both components are mixed in the vessel (see p 2).

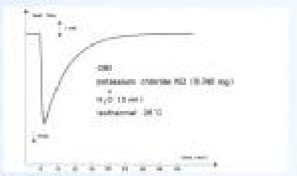
By scanning the temperature in the calorimeter both the curing temperature and heat of the resin are defined. Kinetic use of the peak of polymerization provides isothermal curing simulations.



Decomposition/pressure

Numerous industrial operations conducted in a reactor bring into play major pressures. For maximum personal and material safety a maximum amount of information is required as to how the reaction unfolds so as to be able to direct it better : product stability, risk of decomposition, pressure in the reactor.

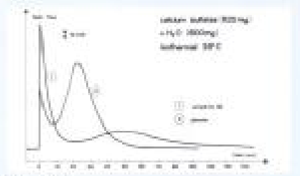
With the **C 80** simulating these operations can easily be carried out in the high-pressure vessel and the required information is found by analyzing the calorimetric and barometric curves (e.g. : decomposition of diterbutyl peroxide in toluene).



Dissolution

Dissolving operations are very common in industrial processes. Simulating this operation in the **C 80** is vital for determining a substance's dissolution rate, for selecting the best solvents based on the results of dissolution and for determining the heat of dissolution.

The dissolution test is also a calibration test for the C 80, which is used in the mixing calorimeter (dissolving potassium chloride in water).

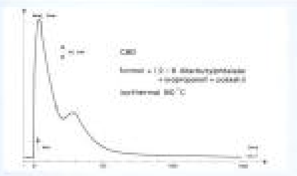


Hydration

Numerous products delivered in a dehydrated state must be rehydrated before use. Such is the case with the varying types of plaster and cement.

The **C 80** is especially appropriate when studying how these products hydrate, as well as how they set when either plaster or cement is brought together with water. This test provides rapid and accurate measurement of the time taken for setting based on the constituents analyzed and the quantities of water added.

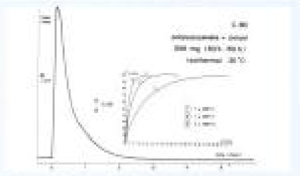
(E.g. : hydration of plaster and calcium anhydride).



Reaction

Select the most appropriate reaction temperature, which is the one providing the greatest savings in energy and measure that the reactor's temperature control and cooling are set so as to prevent a too great temperature rise during the reaction's exothermicity. All these paramaters can be deduced by simulating the reaction produced with the **C 80**.

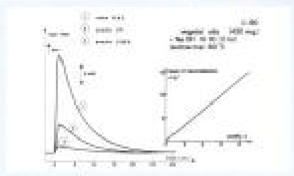
(E.g. : condensation of formaldehyde using 2-6 diterbutyl phtalate brought together with potash, in solution in isopropanol).



Polymerization (mixing)

Numerous polymers are produced by mixing monomers (e.g. : polyurethane by the reaction of polyisocyanate and polyol). By using the membrane vessel on the **C 80** both monomers are initially separated and stabilized at the test temperature in the calorimeter before being mixed.

As monomers are generally viscous mechanical agitation is oftenly needed to provide good mixing.

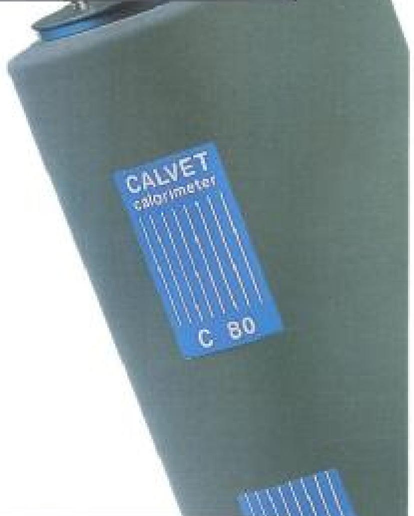


Neutralization

Neutralization is a very common operation in industrial chemistry as well as in other fields such as in the food industry.

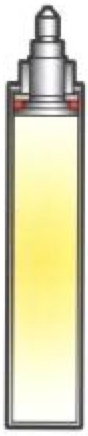
An example is provided by the dosing of the acidity of oils of different origins by using a soda solution.

By measuring the heat of neutralization the calorimetric test accurately determines the oil's acidity and provides useful pieces of information for neutralization when carried out industrially.



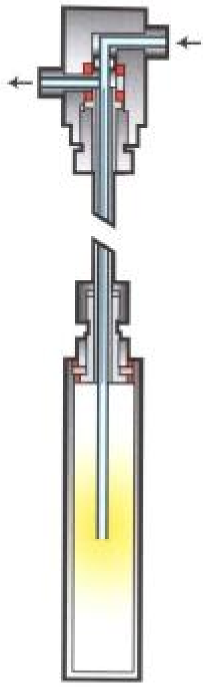
C 80... an impressive range of vessels

Using the **C 80** calorimeter also means selecting the appropriate vessel for the experiment and the sample.
Simulating a reaction or a transformation, having the pressure of the property of the gas vary around the sample, mixing two solids or liquids, these are some of the facilities offered by the vessels in the **C 80.**
Discover the range of vessels in the **C 80**. (For more details you can also refer to applications file n°8).



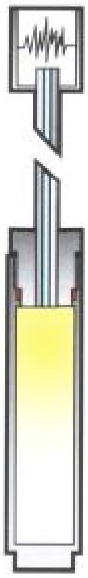
Standard vessel

The standard vessel is designed for heating solids and liquids when studying their types of transformation and setting a thermal balance, when measuring the heat capacity of solids and when simulating reaction and decomposition.
This vessel, made up of a cylindrical container and a cap, is fluid-tight and has no connection with the outside.
It is available in two models : normal pressure (max : 5 bars) and high pressure (max : 100 bars).



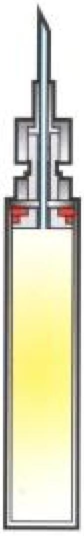
Gas circulation vessel

The gas circulation vessel is used to produce a gas flow (inert or active) around the sample. An inert gas is used to protect the product from possible oxidation, to study pyrolysis of the product and to carry away the vapours given off by the sample as it decomposes. An active gas acts on the product by either oxidizing or reducing it so as to become adsorbed on it.
So as to provide this gas flow the metal container forming the vessels is fitted with two coaxial tubes acting as the inlet and outlet for the gas. It is available in «normal pressure» and «high pressure» versions.



Pressure-transducer-fitted vessel

When a product decomposes, a great amount of vapour is given off and there is rapid pressure rise within the reactor. The value of this pressure needs to be known so as to set up the reactor correctly and provide any safety fittings needed to prevent the danger of explosion or damage.
The high pressure vessel (350 bars) fitted with a pressure transducer provides simultaneous evaluation of the pressure during the reaction and the quantity of heat given off.
The pressure transducer is linked to the vessel (made of Hastelloy C) via a capillary tube containing mercury and silicone oil.
Calorimetric and barometric information is acquired and processed by the computer.
The pressure-tranducer-fitted vessel is especially appropriate for studying how organic products decompose, how auto-catalytic effects can be distinguished, for studying reactions where vapour is given off (polymerization, combustion...) and for experiments on powders, explosives and fuels.



Vacuum vessel

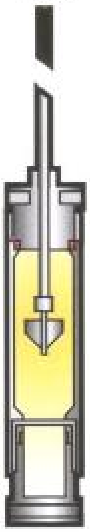
The vessel known as the vacuum one is used for analyzing the sample with a vacuum applied as well as for applying a gas pressure (up to 5 or 100 bars) throughout the experiment. The metal container, forming the vessel, is connected via a tube to the vacuum-applying or pressurising facility. This vessel is available in «normal pressure» (max : 5 bars) and «high pressure» (max : 100 bars) versions.
This vessel is designed for studying decomposition under a vacuum or reduced pressure applied (dehydration, desorption,...) and for studying reactions under pressure (oxidation, reduction, pyrolysis).

Vessel for measuring the heat capacity of liquids

Accuracy in measuring the heat capacity of a liquid by calorimetry depends on a corrective term linked to the presence of a vapour phase above the sample.
To remove this correction the Cp liquid vessel, made up of a metal container capped with a welded tube, is completely filled with liquid via the tube. The special welding of the tube to the vessel prevents any captive air bubbles. When the liquid is heated it freely expands into the tube, but the volume of liquid held in the calorimetric detection area remains the same.
Accurate measurement of the volumic Cp of the liquid is thus carried out, especially by using the step scanning method.

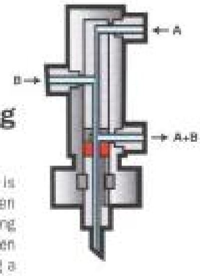
C 80... a range of vessels and applications

Mixing is probably the most widespread industrial operation. So as to simulate the various types of mixing operations involving solids and liquids, the **C 80** calorimeter is fitted with numerous facilities : reversal fitting, mixing vessel using reversal, membrane and liquid circulation vessels, mechanical stirring fitting.



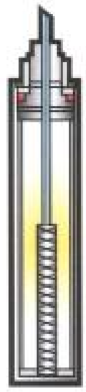
Membrane mixing vessel

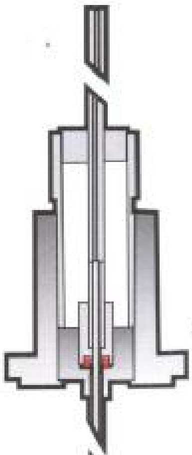
In the membrane mixing vessel the two compartments are separated by a metal or PTFE membrane. After separately introducing the samples into the compartments mixing is done by breaking the membrane using a metal rod, which is operated from outside. This rod is also used to stir the mixture and make it homogeneous.
To make this operation simpler and more easily reproducible a mechanical feature for continuous stirring can be fitted to the vessel. This is specially useful for mixing viscous products (polymerization, organic synthesis).
This vessel is used without the reversal fitting. These applications are identical to those with the mixing vessel using reversal.



Mixing vessel using circulation (»Flow»)

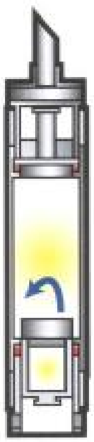
Mixing two liquids in an industrial process is often, a continuous operation, such as when filling reactors with reactive liquids, when mixing two liquid phases in a distillation column, when neutralizing an acid with a base, when titrating a mixture....
The mixing vessel using circulation (»Flow») provides simulation of this operation and evaluation of the heat given off.
The two liquids to be mixed are introduced continuously using peristaltic pumps into the vessel via two inlet tubes.
A static mixer, fitted in the vessel, undertakes mixing of both liquids. The outlet tube provides continuous discharge of the mixture formed.
By varying the inlet flow-rates of both liquids their mixing diagram is determined.





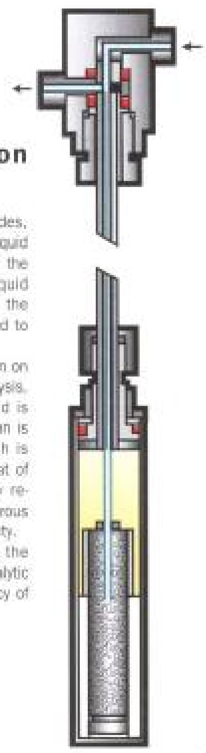
Mixing vessel using reversal

The mixing vessel using reversal is divided into two compartments, each with a variable volume and separated by a mobile metal lid.
The samples (liquid-liquid or liquid-solid) are introduced separately into the vessel. The lid keeps the constituents, as well as any possible vapours from them, fully isolated. Once there is thermal stabilization in the calorimeter reversal of the **C 80** brings together both constituents and makes sure that they mix.
The mixing vessel using reversal is designed for studying liquid mixing (dilution, neutralization, chemical reaction,), and solid-liquid mixing (dissolving, hydration, wetting, reaction).



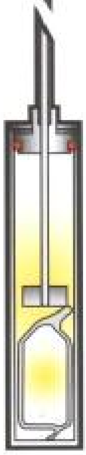
Liquid percolation vessel

Numerous products such as catalysts, oxides, are used for reactions taking place in a liquid environment. Full knowledge is needed for the surface state of these products. The liquid percolation vessel is used to distinguish the adsorption of liquids on such products and to distinguish their reactivity.
The vessel contains a sintered metal section on which is arranged the granulate under analysis.
Using a metal tube an initial carrier liquid is introduced to wet the powder. This operation is followed by introducing the solution which is adsorbed on the powder. Studying the heat of adsorption, and then of desorption (by re-introducing the carrier liquid) provides numerous items of information on the powder's reactivity.
This vessel is appropriate for studying the reactivity of powders, the simulation of catalytic reactions and the measurement of efficiency of exchange ions resins (fixation, elution).



Breakable ampoule vessel (under vaccum)

Sealed under vacuum used for the study of wetting and hydration.



C 80 :
specifications

Temperature

Range : Ambient to 300°C
Temperature scanning : 0.01 at 2°C.min^{-1}
by step of 0.01°C.min^{-1}
Fan-induced cooling.

Vessels

Working volume : cylinder H : 80 mm - Ø : 17 mm.

Vessel types :

- standard (normal and high pressures)
- vacuum (normal and high pressures)
- fluid circulation (normal and high pressures)
- mixing using reversal
- mixing using a membrane
- mixing using mechanical stirring
- mixing liquids by circulation (flow)
- liquid percolation (normal and high pressures)
- liquid Cp
- pressure-transducer-fitted (350 bars/300°C)
- thermal conductivity of fluids
- vaporization
- ampoule vessel

Vessel materials :
stainless steel (Z2 CND 17-12)
hastelloy C

Calorimetric signal

Detection limit : 2 to 5 µW (0.5 to 1.2 µcal·s^{-1}) depending on operating conditions
Time constant : 100 s (empty vessel)
250 s (full vessel)
Calorimeric resolution : 0.1 µW
Joule effect calibration.

Fluids

gases :
static, dynamic,
under pressure (max 100 bars)
inert (argon, nitrogen, helium...)
reactive (oxygen, hydrogen...)

liquid :
dynamic (peristaltic pump)..

The **C 80** is supplied with SETSOFT, SETARAM's thermal analysis package operating via WINDOWS™

Fields of application

Polymers - resins (polymerization, transitions)
Petrochemistry - industrial chemistry (safety, reaction)
Foodstuffs (gel, emulsion).
Biology (fermentation)
Fats (solvatation)
Biochemistry (proteins, enzymes)
Pharmaceutical (reaction, safety)
Petroleum (oil recovery, micelles)
Coal (gasification, liquefaction).
Electrochemistry (batteries)
Pyrotechnics - explosives (ageing)
Storing energy (solar, reaction)
Industrial thermal technology (heat-carrying fluids)
Types of cements and plasters (hydration, setting)
Raw materials and minerals (wetting).

The technical specifications are given as an indication and may be subject to modification by the manufacturer.

SETARAM
Groupe sfim

7, rue de l'Oratoire F-69300 CALUIRE - France
Tel. + 33 (0)4 72 10 25 25 - Fax + 33 (0)4 78 28 63 55

SETARAM
160, boulevard de la République
F-92210 SAINT-CLOUD - France
Tel. + 33 (0)1 47 71 68 33
Fax + 33 (0)1 46 02 76 50

SETARAM SA - Techn. Büro Deutschland
Wilhelm Busch Weg 1
D-63303 DREIEICH - Deutschland
Tel. + 49 (0)6103 322503
Fax + 49 (0)6103 36479

BP 3000