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The CPA102 Reaction Calorimeter

ChemiSens
Reaction Calorimeter Systems

OBJECTIVE

ChemiSens has been working in the field of reaction calorimetry for many years and is specialized in the field of reaction calorimetry where analytical precision is essential.

Based on our experience in precision calorimetric measurements our objective has been to offer reaction calorimeters based on the best measuring principles.

Our reaction calorimeters shows all the facilities that can be expected for process development combined with the versatility of handy laboratory reactors.

APPROACH

Reaction calorimetry is a well established technique within chemical engineering since many years. Traditionally, reaction calorimeters have been build as standard laboratory reactors with an add on of a few extra sensors and an electrical calibration heater.

ChemiSens reaction calorimeters are designed with all considerations to be a precision tool for analysing chemical processes.

The major output from experiments in a reaction calorimeter is the heat production rate, associated with the processes inside the reactor. The heat production curve is then the base for the calculations of a number of important parameters.

The technique to measure and the way to calculate the heat production rate is of utmost importance for the reliability of all related calculations and considerations.

ChemiSens reaction calorimeters are designed and build in a way that makes it possible to pre-calibrate the instruments. The relation between the measured signals and the presented heat production rate is defined by parameters with stable and known values.

RESULT

The engineering efforts have led to the construction of the CPA102 system. The robust and versatile design makes the CPA102 a powerful tool in reaction calorimetry and also a qualified laboratory reactor system for process developement under well defined conditions.

The CPA102 System

A Complete System
The CPA102 is a complete system, designed for extended use in reaction calorimetry, precalibrated and ready to give the answers. The system philosophy is up to date process control.

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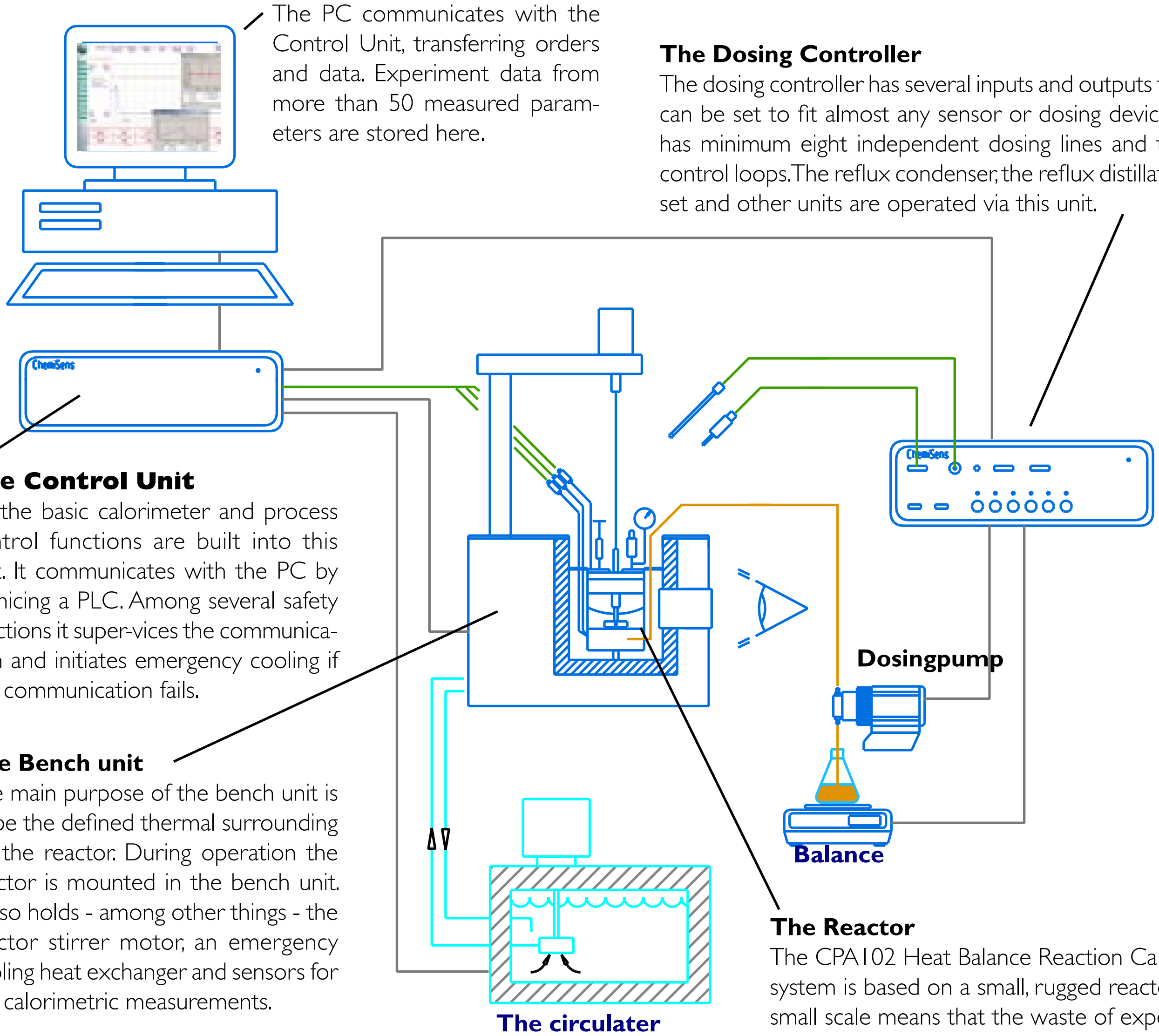
The PC
The PC communicates with the Control Unit, transferring orders and data. Experiment data from more than 50 measured parameters are stored here.

The Dosing Controller
The dosing controller has several inputs and outputs that can be set to fit almost any sensor or dosing device. It has minimum eight independent dosing lines and two control loops. The reflux condenser, the reflux distillation set and other units are operated via this unit.



The Control Unit
All the basic calorimeter and process control functions are built into this unit. It communicates with the PC by mimicing a PLC. Among several safety functions it super-vices the communication and initiates emergency cooling if the communication fails.

The Bench unit
The main purpose of the bench unit is to be the defined thermal surrounding for the reactor. During operation the reactor is mounted in the bench unit. It also holds - among other things - the reactor stirrer motor, an emergency cooling heat exchanger and sensors for the calorimetric measurements.

The Reactor
The CPA102 Heat Balance Reaction Calorimeter system is based on a small, rugged reactor. The small scale means that the waste of expensive chemicals is limited and consequently the disposal of toxic by-products is minimised. A smaller scale means that less energy is accumulated.

Experiment Data
The CPA102 software allows you to run experiments fully automatic or to run some routines automatically while you operate the rest manually.

You specify the parameters of interest to be stored in the experimental log. In the background the system stores all available parameters in a historical log. No data is lossed.

The CPA102 reactor

The standard reactor is a cylindrical, double walled glass vessel. It is capped, top and bottom, with stainless steel. Its special design makes it very handy for the operator. The open vessel can be placed on a balance during the charge of solvents, chemicals etc. The reactor lid holds the shaft-seal and the necessary armature for safety and for charging, evacuation, sampling etc.
During operation the reactor is located in a fixed position in the stainless steel thermostating bench unit, witch also acts as a safety shield.

As standard the reactor is made from stainless steel type 316 in the lid and the base while boro-silicate glass is used for the inner and outer cylindrical enclosures.

The pressure range for the standard version is from vacuum to 20 bars. Optionally to 100 bars. The temperature range is from -20° C to 200° C.

Ports are provided in both the lid and the base for auxiliary probes such as pressure, pH, gas-flow meter etc. The reactor temperature sensor - and maybe the calibration heater - enter the reactor vessel through base ports. The remaining three - or maybe two - baseports can be used for dosing or sampling. All fittings in the lid are compatible with the well-known Swagelok system from Crawford Fittings US.

The reactor volume

The total CPA102 reactor volume is approximately 250 ml where the useful volume ranges from 40 to around 180 ml. With special agitators the reactor can be run with even smaller amounts and still measure with full accuracy.

Safe.

When it comes to handling hazardous processes, which is a normal working field in reaction calorimetry, it is advantageous to have the reactor volume as small as possible. In a small system less energy is accumulated and consequently the worst case scenario is less dramatic.

Economical.

The small volume and the reactor design means that only small amounts of chemicals are needed for "full grown" experiment, important when working with expensive chemicals. It also means that you can make more experiments.

Powerful.

In a series of uniform reactors a smaller volume gives a higher ratio area/volume. With a reacting volume of 40 ml's in the CPA102 reactor a cooling capacity of 500 W/kg is possible.

Scaling up.

The favourable design of the CPA102 reactor makes it as fit for scaling up as traditional 2 litres systems.

Process design.

The CPA102 reaction calorimeter is primary a tool for searching process knowledge and not an apparatus for laboratory production. If laboratory production during precise reaction conditions is required then the 2 litres heat balance system RM200L is the device.

Handy.

The CPA102 reactor is small but still large enough to be very handy and also large enough to allow the use of sensors and equipment commonly used in reaction calorimetry.

The CPA102 standard reactor.

The reactor stirring

Three types of stirrers are used as standard equipment: anchor, turbine and propeller. The stirring speed is controlled in a closed loop and ranges from 50 to 2000 rpm. It can be constant or follow any profile. The stirring power can be estimated from the change in the motor current uptake or measured directly with the optional torque transducer.

For more intensive mixing the reactor accepts the installation of a baffle.

The torque transducer.

The torque transducer is located below the shaft seal and inside the vessel. This means that the correct torque is measured, no friction losses in the shaft seal are included.

A change in the stirring power might reflect a change in the viscosity or indicate an unstable system, fouling or agglomeration.

The reactor temperature control

The CPA102 reactor is a jacketed reactor, where the reactor base-section is used as the heat transfer area. The temperature in the reactor is controlled by adjusting the temperature of the media circulating in the jacket.

The bench unit, surrounding the reactor during operation is thermostated, which ensures that the heat losses are minimised and kept constant. To prevent from reflux inside the reactor during normal operating circumstances, the reactor lid is equipped with an electrical heater. This heater has its own temperature control.

The reactor temperature is measured and controlled in a cascade loop together with the reactor jacket temperature. The temperature control utilises a PID algorithm, meaning that the reactor temperature will reach its set point without any proportional offset.

During isoperibolic mode the reactor temperature is just a measured variable.

Catalyst basket

The versatile CPA102 reactor supports the installation of different auxiliary devices such as a fixed basket for catalysts, ion exchange resins etc.

The measuring principle

The CPA102 reactor is designed to measure according to both the heat balance principle and the heat flow principle. During operation the temperature of the reactor is controlled by adjusting the temperature of the media that passes the reactor base jacket. The temperature difference that arises between the reactor content and the media in the jacket is the driving potential for the heat flow from or into the reactor. This heat flow power can be expressed:

$$\textbf{HF power} = U*A*(Tr-Tj)$$

where U*A is the product of the total heat transfer coefficient U and the wetted area A inside the reactor. The value for U is an experimental parameter, it changes during the reaction and at different stirring intensities. This fact is the major drawback related to the heat flow technique.

All the heat transported out from the reactor will leave via the thermostating media passing the reactor base jacket. A heat balance equation between the outlet and inlet of the thermostating jacket gives:

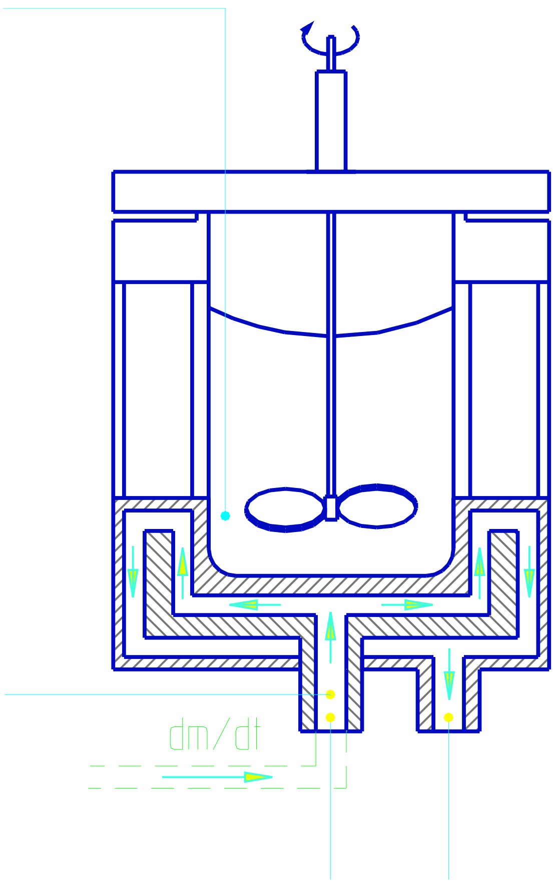
$$\textbf{HB power} = dM/dt*Cp*(Tout - Tin)$$

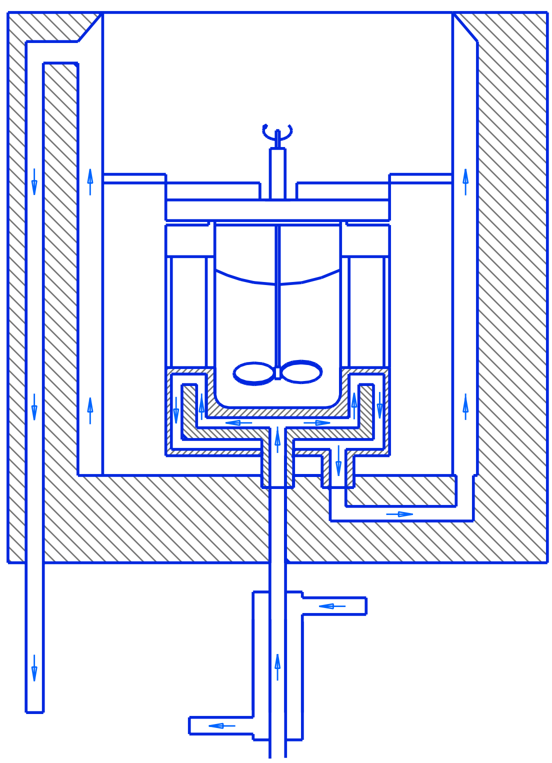
In this equation (Tout – Tin) is the measured temperature difference between the outlet and inlet of the thermostating media to the reactor base jacket. The flow rate (dm/dt) and the heat capacity (Cp) are system properties of the CPA102. They refer to the flow rate and the heat capacity of the used thermostating media. By knowing their values at each operating temperature the thermal power from the process can be directly calculated from the measured temperature difference.

Both the flow rate and the heat capacity are best determined through calibration experiments where known electrical power is generated inside the reactor. From the response in the temperature difference (Tout – Tin) a value for the product is calculated. These calibration experiments can be made in advance and with any media in the reactor.

During the ongoing process in the reactor the CPA102 system uses the calibration data from file to calculate the power. This power is continuously presented.

The possibility to calibrate in advance will significantly reduce the time consumption of most experiments and the measuring principle - heat balance - will eliminate much of the work and errors in the data evaluation.





The CPA102 system - schematic figure

The thermal modes

The CPA102 can be run in different "thermal modes", i.e. isothermal, isoperibolic, temperature scanning and set new temperature.

In the isothermal mode the reactor operates at the temperature set point. The cascade PID/PID temperature control gives no proportional offset at steady state.

Isoperibolic mode means that the temperature set point refers to the reactor base temperature.

Temperature scanning means that the reactor temperature is increased or decreased linearly. The maximum scan rate is +/- 2 deg/min.

Set new temperature means the highest heating or cooling to reach the temperature set point of the instrument.

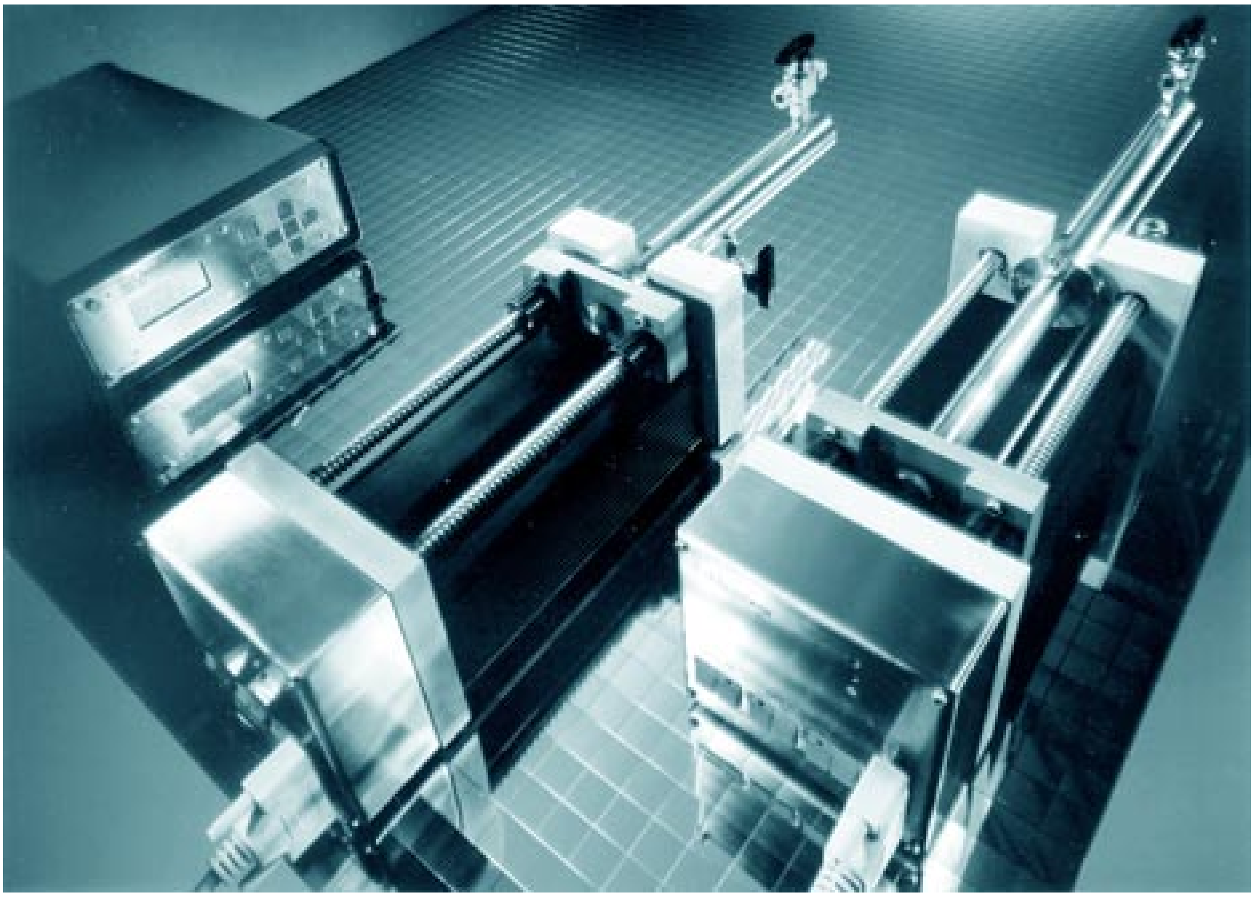
During any of the thermal modes all safety measures are active. The "maximum temperature" limit for the reactor can never be overruled. If the set value is reached the system starts cooling down to the set minimum (safety) temperature for the system.

Dosing

Dosing of chemicals to the reaction calorimeter during the course of a reaction is very essential. Dosing normally means a thermal disturbance. Depending on the reactor temperature the disturbance might be endothermic or exothermic. The technique to handle the disturbance is to measure the temperature at the inlet of the dosing line to the reactor, multiply with the heat capacity and the dosing flow rate and in this way generate a correction term to be used at the post data treatment.

The CPA102 reactor accepts a number of simultaneous dosing lines, solid material, liquid as well as gas. The dosing can reach the reacting system either via the gas phase or direct into the liquid phase.

For very precise dosing flow rates and for the dosing of viscous material the motor syringe system MSC202 (Optional equipment) can be used.



The MSC202 syringe dosing pump.

Other parameters to be measured.

The reaction data from the calorimetric measurements very often need to be complemented with auxiliary parameters such as pH, pressure, spectrophotometric measurements etc.

The special lid for the CPA102 reactor allows the use of a number of standard probes.

Pressure resistant glass- and reference electrodes for pH measurements.

Optional reactor materials

The standard materials for the CPA102 reactor is glass and stainless steel type 316. Many reacting systems require more corrosive resistant reactor material than the 316 SS.

The CPA102 reactor is therefore also available in two tantalum versions. Tantalum has a corrosion resistance close to that of glass. The pressure range for the tantalum reactor is up to 20 bars.

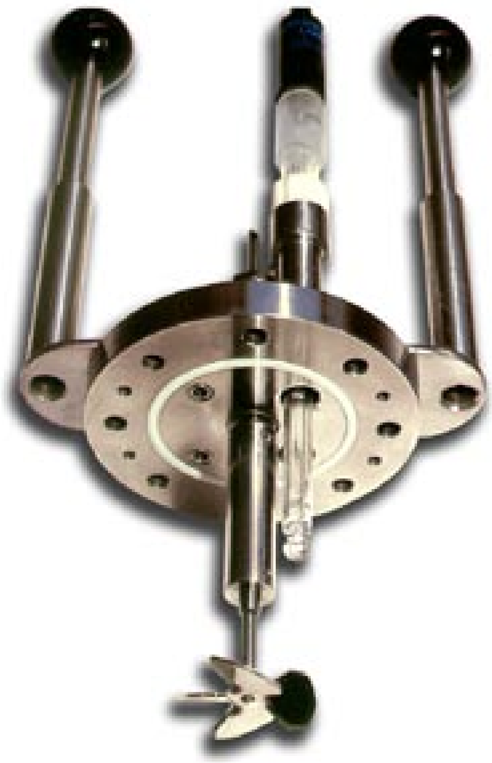
In the full tantalum version all the internal parts that are exposed to the reacting system are made from tantalum. In the semi tantalum version the internal reactor parts that are normally in direct contack with the reacting system are made from tantalum. The other internal reactor parts are made from PFA coated stainless steel.

PFA is a polymer with chemical properties close to that of PTFE.

Higher pressures

The CPA102 reactor is available in a version for 100 bars pressure. This reactor is equipped with a pressurised mechanical shaft seal that uses a seal liquid. The standard reactor material is 316 SS.

Tantalum reactor for pressures up to 20 bars.



The special reactor lid with a standard pH combination electrode mounted

Heat transfer

The heat transfer area in the CPA102 reactor is equal to the reactor base area. This area is always wetted and consequently the heat transfer area is always constant.

If the minimum volume for standard stirrers (around 40 ml) is used, the maximum cooling capacity will reach more than 500 W/litre at optimal conditions and still work accurately. The separate emergency cooling function will considerably increase the cooling capacity if needed.

The internal cooling coil mounted in the special lid.

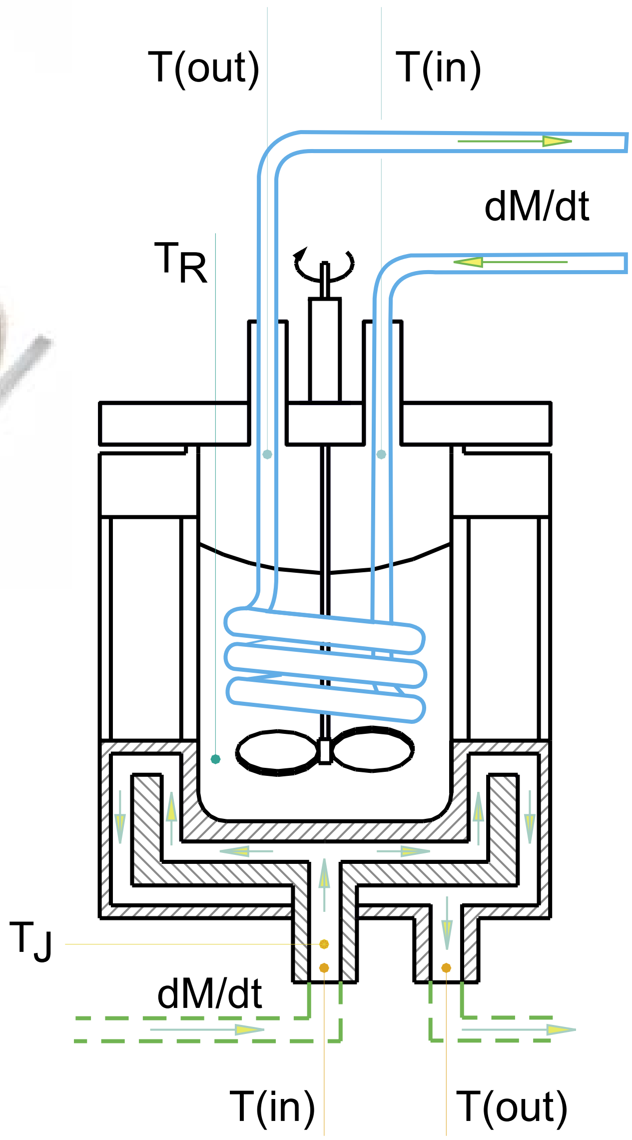
Cooling power boost.

For special applications where the cooling capacity of the standard reactor is insufficient, it is possible to add on an internal cooling coil for increased cooling power. In rough figures a cooling power of 1 kW/litre at temperatures of -20° C is possible.

The power measuring on the additional cooling coil is based on the heat balance principle.

Power = dM/dt*Cp*(Tout – Tin)

The cooling media flow rate is controlled to achieve the desired cooling boost. The total reactor power is then composed of two independent power measurements, i.e. from the build in heat balance measurement of the reactor and the contribution from the heat balance measurements on the cooling coil.



Schematic figure showing the internal cooling coil.

The bench unit.

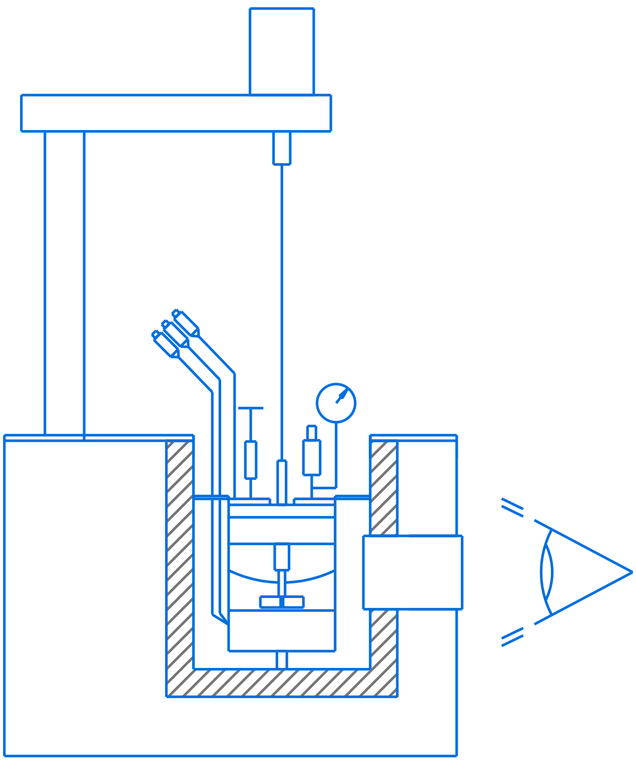
During operation the reactor is always placed in the bench unit. A separate jacket – thermal shield – in the bench unit surrounds the reactor. The thermal shield is not only necessary for precise calorimetry, it also serves as an efficient safety shield in case of a glass jacket burst. An outer circulation thermostat controls the temperature of both the reactor and the thermal shield. The same thermostating media is forced first through the reactor jacket and then through the thermal shield. By this technique the thermal shield will have a temperature very close to that of the reactor jacket and the heat losses will thus be minimised. The circulator requires external cooling, which for a restricted temperature range might be process water.

In the front wall of the bench unit a double walled sight glass is placed. The build in light source together with the sight glass, make it possible to visible follow the process inside the reactor.

The reactor is lifted into the bench unit through an opening in its top plate. The unions for the thermostating media will automatically be connected to the reactor base, when the reactor is installed. The reactor is kept in place just by the gravity.

The bench unit also holds a build in heat exchanger for rapid emergency cooling. This heat exchanger requires an external cooling source. For the temperatures above 35-40° C process water can be the cooling source, otherwise a refrigerating system is required.

The holder for the reactor stirring motor is located on top of the thermostat. Via the shaft extension it is connected to the shaft seal on the reactor lid.



Schematic figure of the CPA102 bench unit.

The CPA102 thermostating unit

The control unit

The control unit is the interface between the operators PC and calorimetric system and its all facilities.

It is a stand alone unit to be placed at a distance up to 10 metres from the thermostating unit and the reactor. The unit holds all the interfacing electronics with its distributed computer system. The safety measures and the control loops and control functions that are time critical for the total system performance are located to the control unit.

To the operator it is a "black box" with a power on/off switch. All cable connectors are located to the rear panel. A separate "panic button" to be placed at a distance from the control unit can be pressed by the operator at any time to instantly activate emergency cooling.

The dosing controller VRC200

All type of dosing controlled by the system is handled via the VRC200. This is a dosing controller to be installed between the CPA102 control unit and almost any type of dosing device, pumps, valves, gas flow regulators etc. If balances are installed closed loop dosing can be used. VRC200 can besides these dosing lines also handle dosing from six other dosing lines, if precalibrated pumps are used.

The VRC200 is also used when auxiliary sensors as pressure, pH, gas flow meters, etc are needed. The versatility of the VRC200 can optionally be further increased by the installation of modules for control of additional specific pumps, reflux condenser, reflux/distillation set, etc.

Reflux operation

The CPA102 reactor can be used with either a pressure resistent reflux condenser or a full reflux/distillation set including a distillation column with thermal measurements. Both type of equipment increase the system cooling power considerably.

The condensers utilise the heat balance principle for the power measurements. To compensate for the heat losses the condensers also include separate sensors to measure the heat flow that escape through the insulation of the condenser.

Power = dM/dt*Cp*(Tout – Tin)

Flow control unit with integrated flow sensor. Used together with reflux condenser

Pressure resistant- 20 bars - reflux condenser with HeatBalance measurement.

Safety measures.

The CPA102 system is build to ensure high operator safety during all operational conditions.
The system includes both software controlled and hardware controlled safety functions. The basic idea is that the hardware functions are operating on a lower system level and can never be overruled by the computer system.

Maximum and minimum temperatures.

The operator must always specify the highest acceptable reactor temperature and the minimum temperature. The minimum temperature is a temperature that is considered as a safe temperature i.e. no reaction will take place.
If the reactor temperature during an experiment reaches the maximum temperature, the system will interrupt all dosing and use the maximum cooling power to reach the minimum temperature.

Hardware controlled maximum temperature.

This temperature is set directly on the external circulator and refers to the temperature of the thermostating media in the reactor jacket. The temperature in the circulator will be limited to this value.

Watchdog.

A separate circuit – the watch dog – supervises the computer control of the CPA102 system.
If the communication between the CPA102 control unit and the operators PC is interrupted or the internal computer system in the control unit fails a hardware controlled emergency cooling is initiated.

Emergency cooling.

The operator always has direct access to the emergency cooling function by pressing a "panic button" which can be located at a convenient operator place.

Other parameters.

All measured parameters by the system can be used single or in any multiple combination to generate any action that is accessible by the present system configuration.

Internal safety measures.

All important internal functions of the system are also supervised and in case of critical failures automatically appropriate actions are taken.

Ex.:

Reactor stirrer overload protection
Supervision of thermostating media level
Protections against hazardous temperatures via separate circuits.
Protection of calibration heater from internal over-temperature
Supervision of temperature sensor characteristics
Supervision of critical electronic functions (A/D conversion etc.)
Supervision of temperature of internal critical components
Supervision of different dosing functions

Measured parameters.

The CPA102 system is run via a dedicated application of the InTouch software from Wonderware US. The ChemiSens application is called ChemiCall and offers some 50 measured parameters. All of the parameters are available on-line and most of them can be used on-line as test parameters for conditional jumps in automated, programmed experiments. The embedded graphic controller enables the possibility to manipulate any parameter to create user defined presentation of the result. All graphic captures, operator notes, events marks and event logs are stored for later use in the ChemiCall report generator. Raw-data can also be exported for use in spread sheet programs as well as the complete report can be exported to be included in other standard documents.

The Heat Balance power from the reactor
The stirring power (torque transducer)
The stirrer speed
The power from the internal cooling coil (opt. equipment)
The reactor temperature
The jacket temperature
The time derivative of the reactor temperature
The calibration power
The readings from two balances
The readings from two pH meters
The readings from two pressure transducers
The readings from four auxiliary sensors
The dosed amount of eight (or more) components.
The Heat Balance signal from the reflux condenser.
The control signal from two control loops.

CPA102 Technical specification

The reactor

Standard material:	316 SS, Borosilicate glass, PTFE and FPM or FFPM elastomers.	
Optional material:	Tantalum instead of 316 SS for wetted parts.	
Total volume:	0.25 litres	
Useful volume:	0.04 to 0.18 litres	
Pressure range:	Standard - Vacuum to 2 Mpa or 20 bars. Optional - Vacuum to 10 Mpa or 100 bars.	
Fittings:	Lid fittings compatible with the Swagelok system.	
Thermal operating modes:	Isothermal, isopheribolic, temperature scanning and "set new temperature".	
Measuring principle:	Heat Balance and Heat Flow	
Temperature range:	-20°C to +200°C	
Temperature resolution:	0.001°C	
Temperature accuracy:	IEC 751 (1/3)	
Power measurements:	Heat Balance	Instrumental resolution +/- 0.05 W Baseline stability normal conditions +/- 0.2 W
	Heat Flow	Instrumental resolution +/- 0.01 W Baseline stability normal conditions +/- 0.05 W Instrumental time constant 15 s
Stirring speed:	Range 50 to 2000 rpm. Constant or any ramp. Max torque 0.1 Nm	
Torque transducer:	Resolution 0.01 Watt. Max torque 22 mNm	

The Bench unit

Physical dimensions:	Height	850mm (without reflux/dest. set)
	Width	300 mm
	Depth	400 mm

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