
CPA 202
Reaction Calorimeter Systems
“Measuring the truth in chemical processes is our obsession”

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.

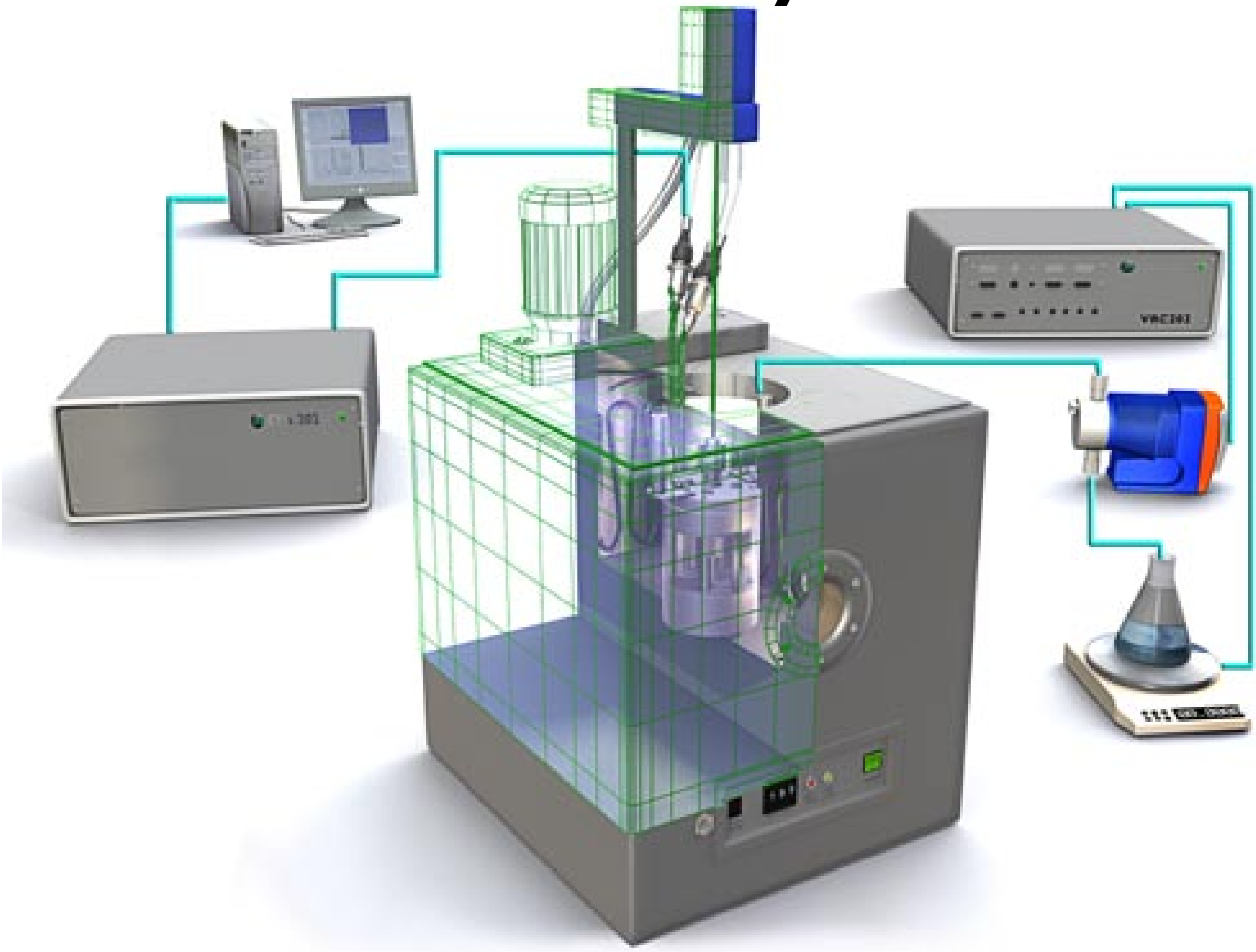
ChemiSens reaction calorimeters are precalibrated, which means that the instrument directly on line presents the heat production rate. The result is absolute, it is never influenced by any doubt from the operator how to interpret calibration pulses or how to estimate unknown baselines.

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 CPA202 system.

The CPA202 Reaction Calorimeter System.



A Complete System
The CPA202 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.

The operator interface
You control your CPA202 system via the user-friendly Human Machine Interface (HMI). The advanced software in the PC allows manual as well as automatic experiments. The software package in the PC is a dedicated application of the HMI "InTouch" (trade name for Wonderware, USA). It is an open system that can be tuned to any need. Having built-in network and internet capabilities it can be extended to include the world.

The Reactor
The heart of the system is the small, versatile and very handy reactor. The built-in, powerful temperature control cooperates with the thermostating unit to allow accurate isothermal, true scanning, adiabatic and "storage test" sessions.

The thermostating unit
The thermostating unit is in itself a precision instrument. It is the defined thermal surrounding for the reactor. It is the thermal shield that allows the reactor to work as a reaction calorimeter rather than being just a handy laboratory reactor.

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

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 handled via this unit.

Experiment data
The CPA 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 the historical log. No data is lost.

The CPA202 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 bath, with also acts as a safety shield.

As standard the reactor lid and base are made from stainless steel 316 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. Ports are provided in both the lid and the base for auxiliary probes such as pressure, pH, gas flow meter etc. All fittings in the lid are compatible with the well known Swagelok system from Crawford Fittings US.

The reactor volume

The total CPA 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. This is different from traditional reaction calorimeters which usually are based on 2 litres laboratory reactors.

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 entrapped 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 experiment. The efficiency of the CPA202 gives you that extra time.

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 CPA202 reactor a cooling capacity of significantly more than 500 W/kg is possible.

Scaling up.

The favourable design of the CPA202 reactor makes it as fit for scaling up as traditional 2 litres systems.

Laboratory production.

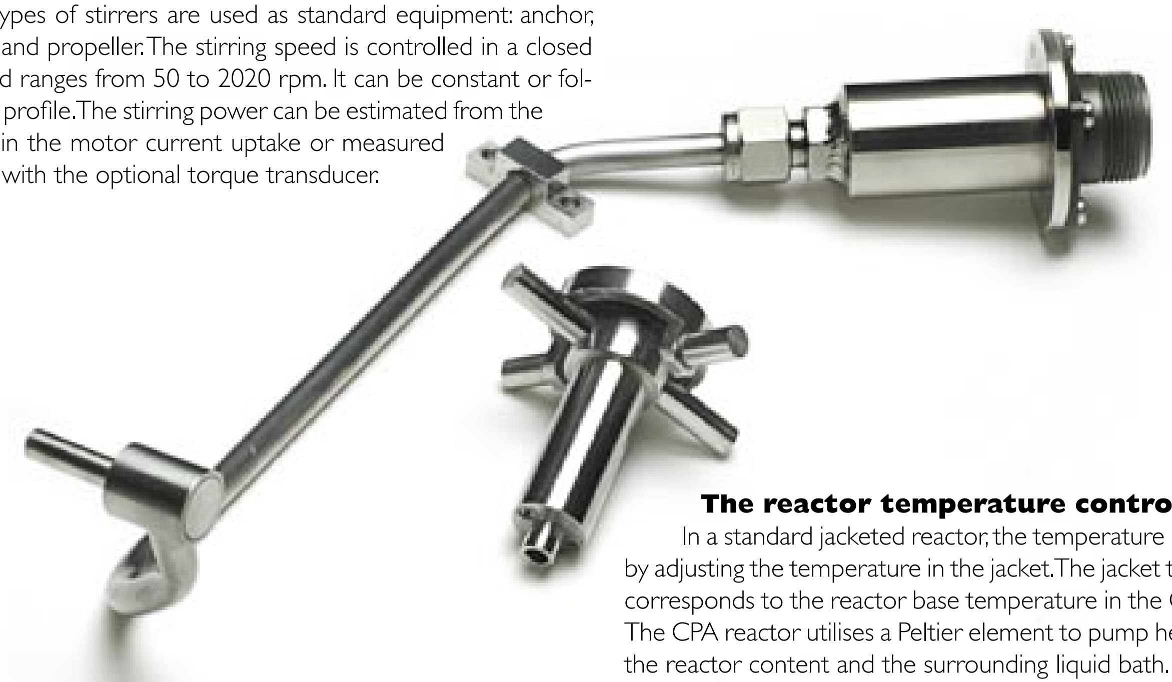
The CPA202 is much calorimeter but it is not ideal for laboratory production of larger amounts. If laboratory production during precise reaction conditions is required then the 2 litres heat balance system Cpa122 is the device.

Handy.

The CPA202 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 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 2020 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.



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.

Catalyst basket

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

The reactor temperature control

In a standard jacketed reactor, the temperature is controlled by adjusting the temperature in the jacket. The jacket temperature corresponds to the reactor base temperature in the CPA reactor. The CPA reactor utilises a Peltier element to pump heat between the reactor content and the surrounding liquid bath.

The thermostating bath surrounding the reactor during operation is always kept at a temperature slightly higher than the reactor temperature. This ensures that during normal circumstances no internal reflux in the reactor will occur.

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

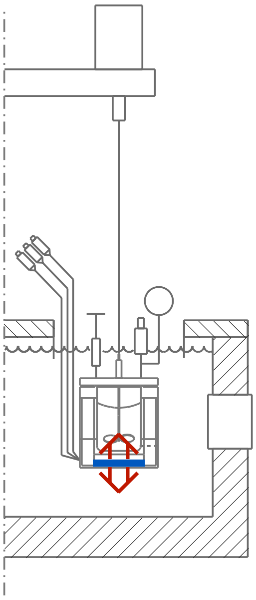
During isoperibolic mode or adiabatic mode the reactor temperature can be seen as a measured variable.

The Heat Flow measurement.

The CPA202 is all the way designed to be a reaction calorimeter as well as a laboratory reactor. It is not a converted laboratory reactor. The CPA202 has been designed in accordance with good calorimeter principles.

Any heat loss is minimised to a level below significance. No heat can enter or leave the system without being detected and measured, i.e. no "base line" guessing.

The heat flow measurement is absolute. The CPA202 is precalibrated just like a mass flow meter or an ampere meter is precalibrated.



Heat is an extensive quantity just like mass and electrical charge but it can not easily be encapsulated. Heat will always dissipate along any existing temperature gradient in the system. The heat dissipation can be minimised by insulation. Active insulation means that the temperature gradients are eliminated by controlling the "outside" temperature to that of the "inside". Passive insulation means adding an outer layer of low thermal conductivity.

A perfect calorimeter should be designed in a way where all heat that leaves or enters the system flows via a dedicated heat transfer area where it is measured.

During operation the CPA reactor is submerged in the thermostating liquid in the thermostating unit. The surrounding liquid has its own control system that keeps the temperature slightly above the reactor temperature. This means an active insulation also of the upper metal parts of the reactor.

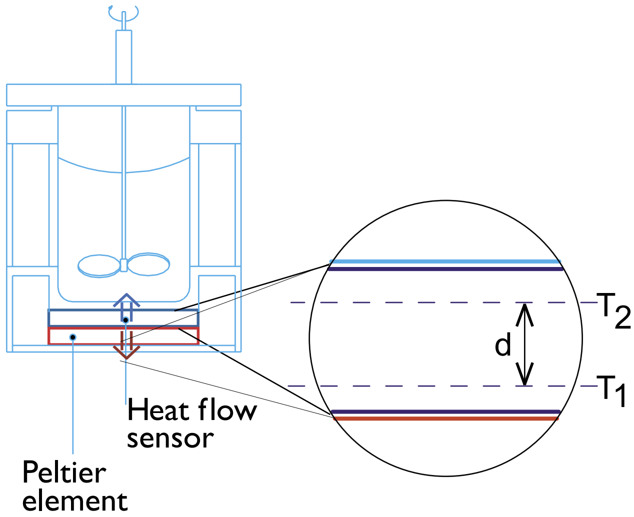
The midsection of the reactor has an outer jacket i.e. it is both passive and active insulated. All heat that is exchanged between the CPA and the surrounding heat sink flows through the reactor base. In all areas of the reactor base where heat flows, independent heat flow sensors are installed. The main heat flow sensor described below illustrates the principle.

A Peltier element is used for the separate temperature control of the reactor. All heat generated in the reactor is transferred out from the reactor and absorbed by the liquid in the thermostating unit. The Peltier element creates the temperature difference that makes the heat flow.

The heat flow sensors.

The main heat flow sensor is installed between the reactor base and the Peltier element. Separate heat flow sensors are integrated in the reactor base wall. The heat flow that is forced through a sensor will create a small temperature gradient difference.

The thermal conductivity of the metals in the heat flow sensor is well known and the heat flow can be calculated according to the equation below.



$$\text{Heat Flow} = \lambda * \frac{A}{d} * (T_2 - T_1)$$

λ = the specific heat conductivity

A = the heat transfer area

d = thickness

The Peltier element.

The thermocouple effect - discovered 1821 by Seebeck - is the fact that an electric current will flow in a continuous circuit of two metals (thermocouple) if the two junctions are at different temperatures. The Peltier effect is the reverse to this. If a current is forced through a pair of thermo couples a temperature difference will arise between the two junctions. The Peltier element used in the CPA202 reactor is a pile of very efficient semiconductor thermo couples arranged between two ceramic plates. When a current passes such an element one side gets warm and the other gets cold. When the reactor needs cooling the cold side of the Peltier element will absorb heat from the reactor base and the hot side will deliver this heat to the reference. If the direction of the current is reversed the cold and hot side of the element will also reverse and the Peltier element will pump heat into the reactor.

The Peltier element used for heating/cooling has nothing to do with the measuring principle, it is just a convenient way to control the temperature in a small reaction calorimeter.

The thermal modes

The CPA202 can be run in different "thermal modes", i.e. isothermal, isoperibolic, adiabatic, scanning, low power 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.

Adiabatic mode permits simulation of large scale reactors. Automatic correction for the reactor's heat capacity, gives the real temperature increase of the reactor contents.

When the temperature increase reaches 4 deg/min the system changes the mode into isothermal.

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

Low power is a special isothermal mode for processes where high resolution and low noise is more important than high cooling power.

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

During any thermal mode all safety measures are active. The maximum power 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.

Special feature of the CPA reactor

Dosing of chemicals to the reaction calorimeter during the course of reaction is very essential. Dosing normally means a thermal disturbance. Depending of the reactor temperature the disturbance might be endothermic or exothermic. The traditional 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 CPA working principle adds on a excellent possibility for all dosed liquid chemicals that are thermally stable at the reactor temperature.

The dosed chemical is easily heat exchanged against the surrounding thermostated liquid before it enters the reactor. No disturbance will be noticed and the power on the screen will still be the evolved power inside the reactor.

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

Heated dosing cylinders. Used to pre-heat highly viscous or solid/melting materia

Ph measurement

Pressure resistant glass- and reference electrodes for pH measurements.

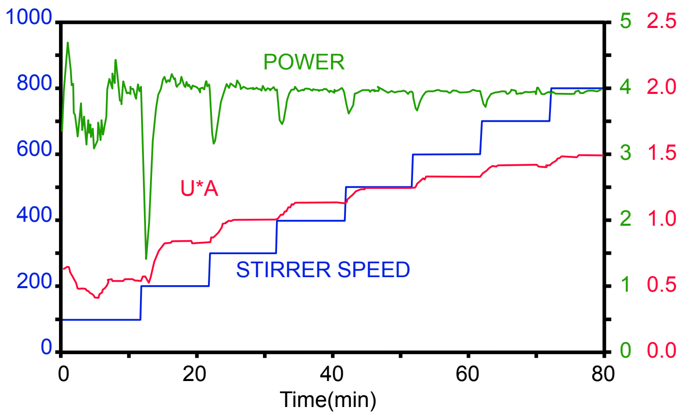
Tantalum reactor for pressures up to 20 bars.

Heat transfer

The heat transfer area in the CPA 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 750 W/litre for optimal conditions.

The figure below shows the measured power (W), the total heat transfer (U*A(W/K)) and the stirring speed (rpm) when a constant electrical power of 4 W was generated in the reactor which contained 100 ml of water. The agitator was a small propeller - at 100 rpm there is practillay no agitation. Also at 800 rpm the agitation is rather poor.



The CPA202 reactor lid with a standard pH combination electrode mounted.

The internal cooling coil mounted in the special lid.

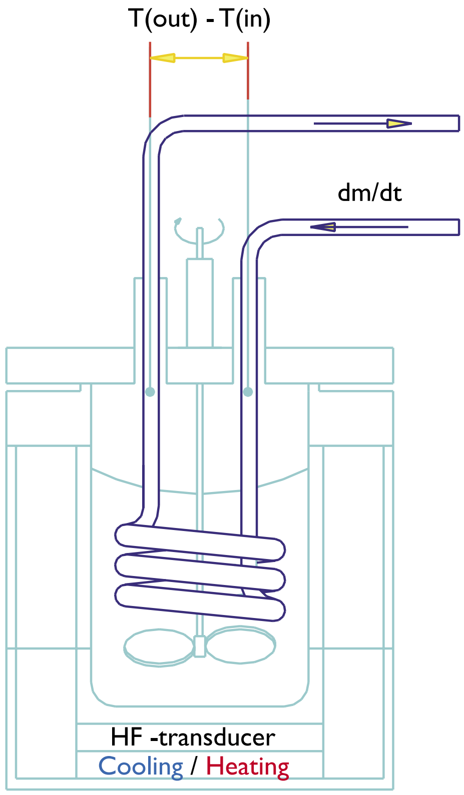
Cooling power boost.

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 -50° C is possible.

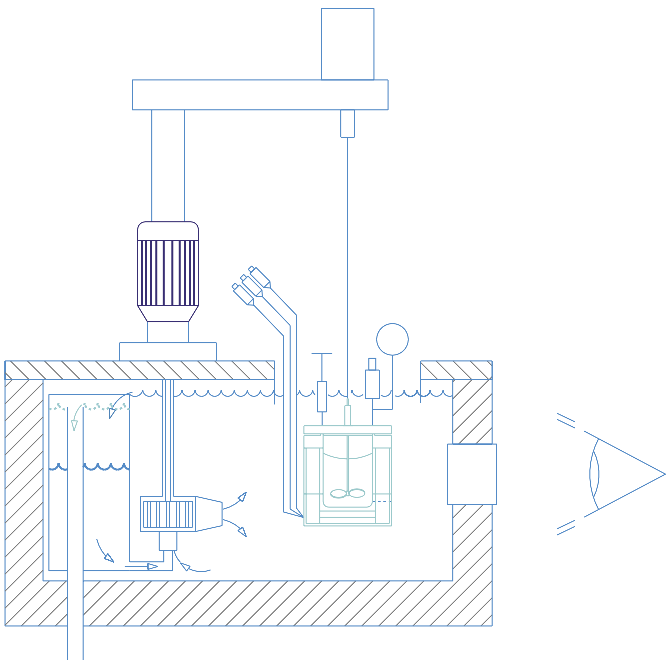
The power measuring on the additional cooling coil is based on the heat balance principle.

The total reactor power is then composed of the power measurements from the build in heat flow transducer in the reactor base and the contribution from the heat balance measurements on the cooling coil.

$$Power = dm/dt*Cp*(T(out)-T(in))$$



Schematic figure showing the internal cooling coil



Schematic figure of the CPA202 thermostating unit also showing the active level control.

The thermostating unit.

During operation the reactor is positioned in the thermostating unit, a heat sink, that absorbs the heat withdrawn by the Peltier element. The thermostating unit also serves as a the thermal surrounding for the reactor which is essential for precise calorimetric measurements.

The thermostating unit is a precision liquid thermostat with a volume of approximately 13 litres. In its front wall there is a double walled sight glass. A build in light source, together with the sight glass, make it possible to visually follow the process inside the reactor.

The reactor is lifted into the thermostat through an opening in the thermostat top cover. To compensate for the displaced liquid volume when the reactor is lifted in or out from the thermostat, there is an internal liquid compensation tank with its own filling pump.

Using a water miscible liquid in the thermostat will keep the reacting system clearly visible even at the lowest temperature -50° C. The thermostating unit requires an external cooling source. Process water can be used but a refrigerating circulator is needed to reach the low temperatures.

The holder for the reactor stirring motor is located on top of the thermostat. The shaft extension connects the stirrer motor with the shaft seal on the reactor lid.

The CPA202 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. All safety measures and all 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 VRC202

All type of dosing controlled by the system is handled via the VRC202. This is a dosing controller to be installed between the CPA202 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. VRC202 can besides these dosing lines also handle dosing from six other dosing lines, if precalibrated pumps are used.

The VRC202 is also used when auxiliary sensors as pressure, pH, gas flow meters, etc are needed. The versatility of the VRC202 can optionally be further increased by the installation of modules for control of additional specific pumps, reflux condenser, reflux/distillation set, etc.

The VRC202 holds facilities for control of almost any measured quantity including operation under constant reactor power. This feature allows the determination of the dosing profile to achieve a predetermined reactor power level.

Pressure resistant- 20 bars - reflux condenser with Heat-Balance measurement

Power = dm/dt*Cp*(T(out)-T(in))

Reflux operation

The CPA 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 through the insulation of the condenser.

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

Safety measures.

The CPA202 system is build to ensure high operator safety during all operational conditions.

The small reactor volume means built-in intrinsic safety but several other safety measures are implemented in the system.

There are the 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.

Maximum reactor power.

When the specified maximum reactor power is reached the system will interrupt all dosing and cool down to the minimum temperature.

Hardware controlled maximum temperature.

This temperature is set directly on the thermostat and refers to the temperature of the thermostating liquid surrounding the reactor. If it is exceeded, the heating is disabled and must be rearmed manually.

Watchdog.

A separate circuit – the watch dog – supervises the computer control of the CPA202 system.

If the communication between the CPA 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
- Circulating pump overload protection
- Liquid level supervised
- Hazardous temperature protected via melting fuse
- Calibration heater protected 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 CPA202 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. Rawdata 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 total power and the true heat flow from the reactor.
The stirring power (torque transducer).
The stirrer motor current.
The power from the internal cooling coil.
The stirrer speed.
The total heat transfer (U*A) value.
The reactor temperature.
The reference temperature.
The time derivative of the reactor temperature.
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 (ore more) components.
The HeatBalance signal, the cooling media flow rate and six important temperature in the distillation set.
The conversion, i.e. the integral of the reactor total power.
The control signal from two control loops.

Applications.

Reaction calorimetry is the tool for real process development and is best demonstrated with realistic experiments.
With a precalibrated reactor like the CPA you can interrupt your experiment anywhere along the reaction course and still have fully correct data for the process. You don't have to wait for the final baseline on a level where you estimate the is completed.

The true power signal directly - and on-line - informs if something is going abnormal and the experiment should be terminated in advance.

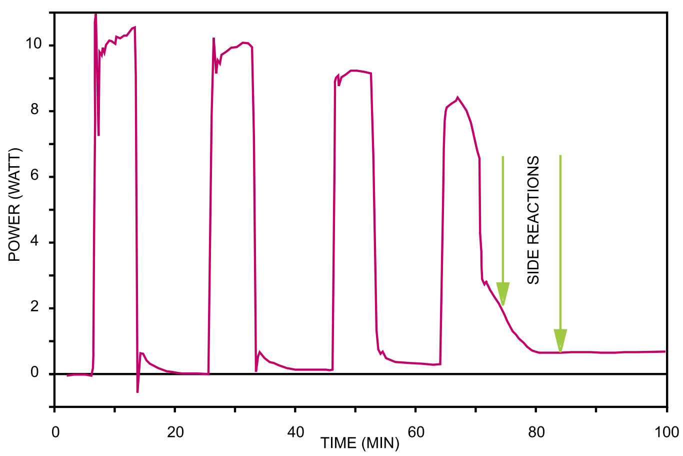
Preparation of 2-ethylhexanol-nitrate.

The reactor was initially filled with a mixture of sulphuric acid and nitric acid. 2-ethylhexanol was step by step added until an end concentration of 1:1 to the nitric acid. The figure shows the initially pure ester formation and the proceeding increase of side reactions upon alcohol addition. Especially the level of slow side reactions at changing molar ratios can be determined accurately.

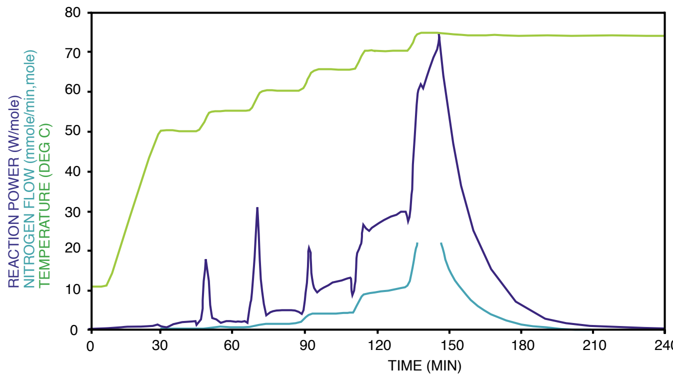
Decomposition of a diazonium compound.

Diazonium compounds are unstable and decompose during the evolution of nitrogen gas.

Details concerning this reaction are important before scaling up. The precalibration of the CPA means that you in one single experiment just by step by step increase the temperature, record the power output and then you have all the data for the Arrhenius plot available. If a gas-flow meter is installed, which is directly supported by the VRC20 the evolved gas can be measured and used to conclude that the thermal reaction investigated is only the decomposition with production of nitrogen.



Preparation of 2-ethylhexanol-nitrate.



Decomposition of a diazonium compound.

CPA202 Technical specification

The reactor:

Standard material:	316SS, Boro silicate glass, PTFE and FPM or FFPM elastomers.
Optional material:	Tantalum instead of 316SS for wetted parts.
Total volume:	0.25 litres
Useful volume:	0.04 to 0.18 litres
Pressure range:	Standard - Vacuum to 2 Mpa, optional - Vacuum to 10 Mpa.
Fittings:	Lid fittings compatible with the Swagelok system.
Thermal operating modes:	Isothermal, isoperibolic, adiabatic, temperature scanning, low power and temperature transport
Measuring principle:	True heat flow. The reactor constructed to exchange heat via the reactor base only. The flow of heat through the base is measured. Calibration is independent of the reactor content volume and the heat transfer properties.
Temperature range:	-50°C to +200°C
Temperature resolution:	0.001°C
Temperature accuracy:	IEC 751 (1/3)
Heat measurements:	# Smallest detectable amount of heat - 2 Joule
	# Precision - The standard deviation between 5 repeated electrical power pulses. 5 Watt during 300 sec. Better than 1 %.
	# Accuracy - Better than 99 % at optimal conditions.
Power measurements:	# Range 0 to +/- 30 Watt, optimal conditions.
Isothermal mode	# Linearity calculated as the deviation from the best straight line between 0 to 30 Watt electrical power. Better than 1 %.
	# Resolution 0.01 Watt
	# Base line drift 8 hours normal lab. conditions 0.02 Watt
	# Precision - Standard deviation of the amplitude mean values of five repeated 5 Watt pulses . Measuring period 5 min with start 2 min after power on. Better than 1 %.
	# Time response - Time to 90 % of final value at a 5 Watt electrical power step - 50 sec.
Stirring:	50 to 2000 rpm. Constant or any ramp. Max torque 0.1 Nm
Torque transducer:	Resolution 0.01 Watt. Max torque 22 mNm

The Thermostating Unit:

Material:	Stainless steel
Volume:	13 litres
Heating Power:	5000 Watt.
Voltage	400 V 2~N +/- 10 %
	alt. 230 V 3~ +/- 10 %
	alt 230 V ~ N +/- 10 % (Reduced power 2000 Watt)
Frequency	50 - 60 Hz
Power consumption:	Max 5200 Watt (2200 Watt), recommended line fuse 16 A
Physical dimensions:	Height (without reflux/dest. set) 910 mm, Width 400 mm, Depth 600 mm
Ambient temperature:	10 to 35° C no condensing

Subject to technical changes. ChemiSens , Lund , Sweden 2004-05-03

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