Small-scale reactor for data oriented process development

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Safety and
Environmental
Technology Group

Background

- Determination of **reaction enthalpies** is crucial:

  - maintain **safe operating conditions** (avoid runaway reactions, excessive heat production, etc)
  - allow prediction of **thermal behaviour**
  - increased **chemical understanding** (information about bond energies, structure, etc)

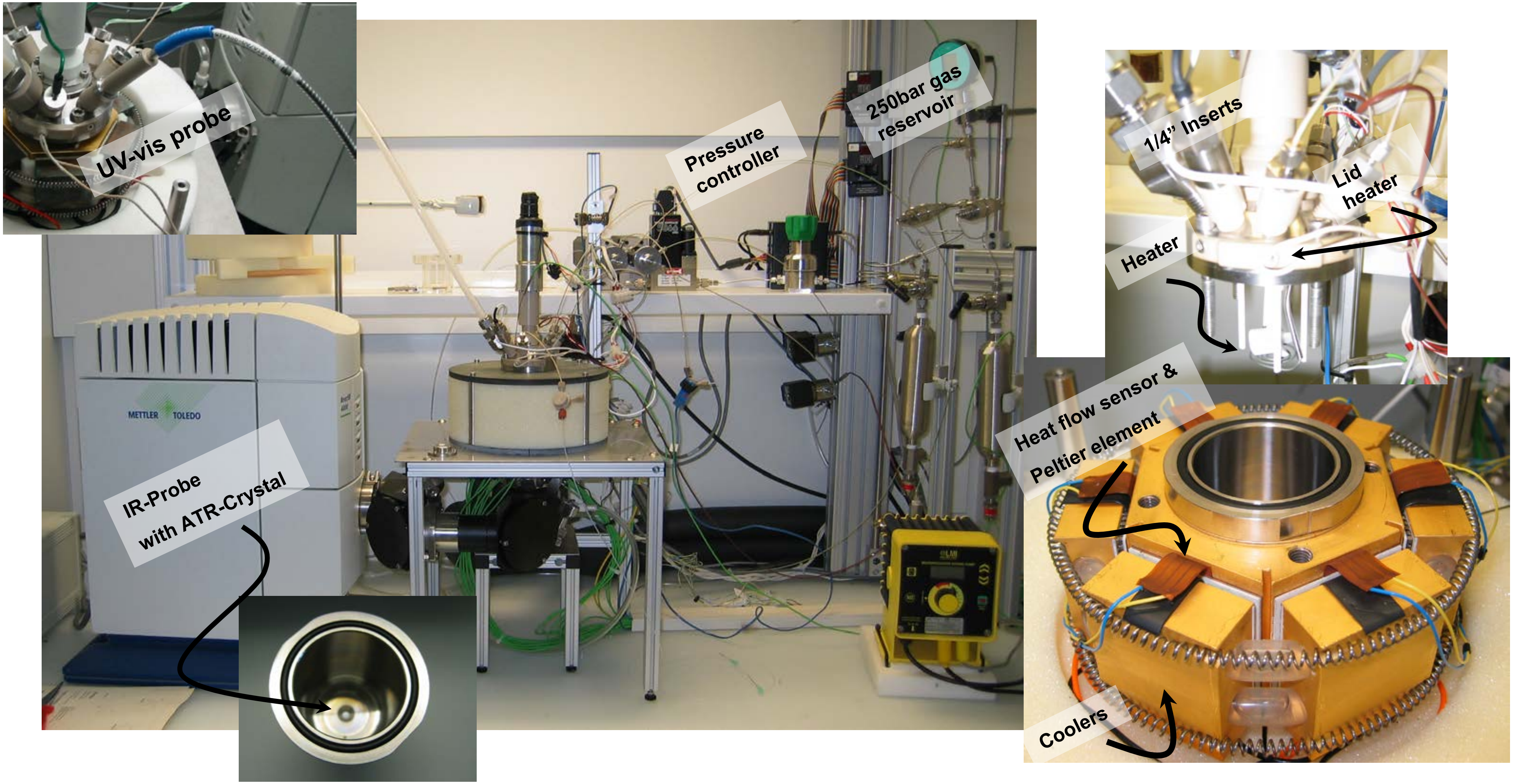
- Determination of **reaction mechanisms** and their associated **rate and equilibrium constants** is crucial:

  - optimisation of reaction conditions for **productivity, efficiency**, **waste minimisation** and **detection of process upsets**
  - increased **chemical understanding**

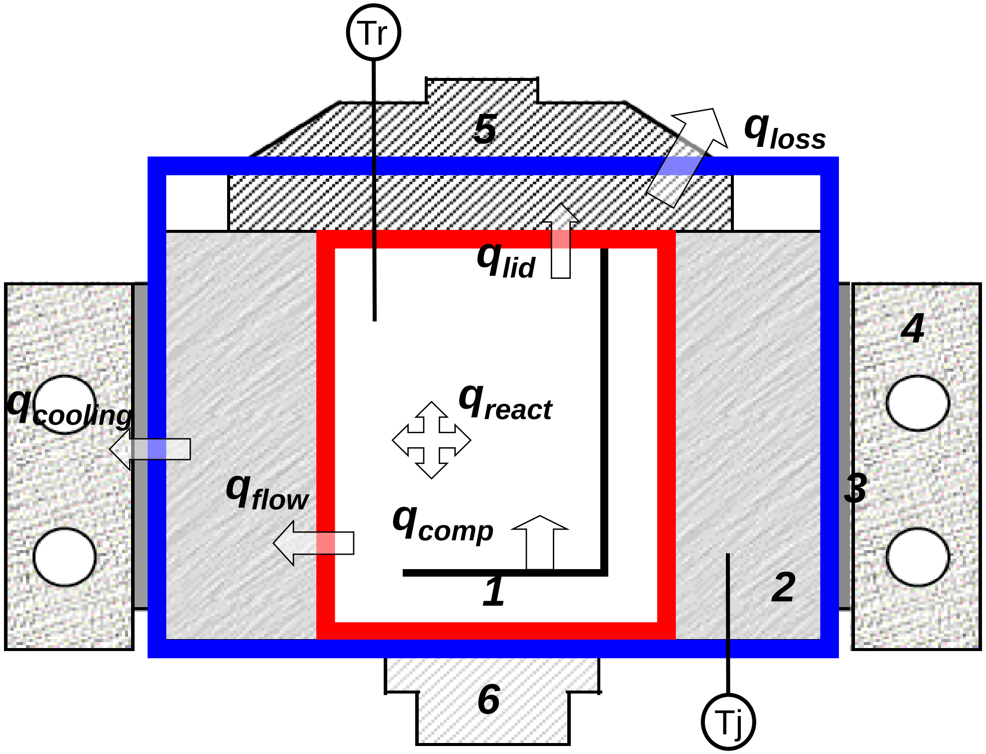
Topics

- Reactor Development
- Chemistry Applications
- Data Analysis

Reactor Development



Calorimetry Measurement Principle



Inner heat balance

$$q_{React} = q_{Flow} - q_{Comp} + q_{Lid} - q_{Dos}$$

Outer heat balance

$$q_{Cooling} = q_{Flow} + q_{Lid} - q_{Loss}$$

1: Compensation Heater
2: Metal Jacket
3: Peltier Element and heat flow sensors
4: Cooler
5: Lid
6: IR Probe

$$q_{React} = q_{Los} + q_{Cooling} - q_{Comp} - q_{Dos}$$

Reactor Specifications

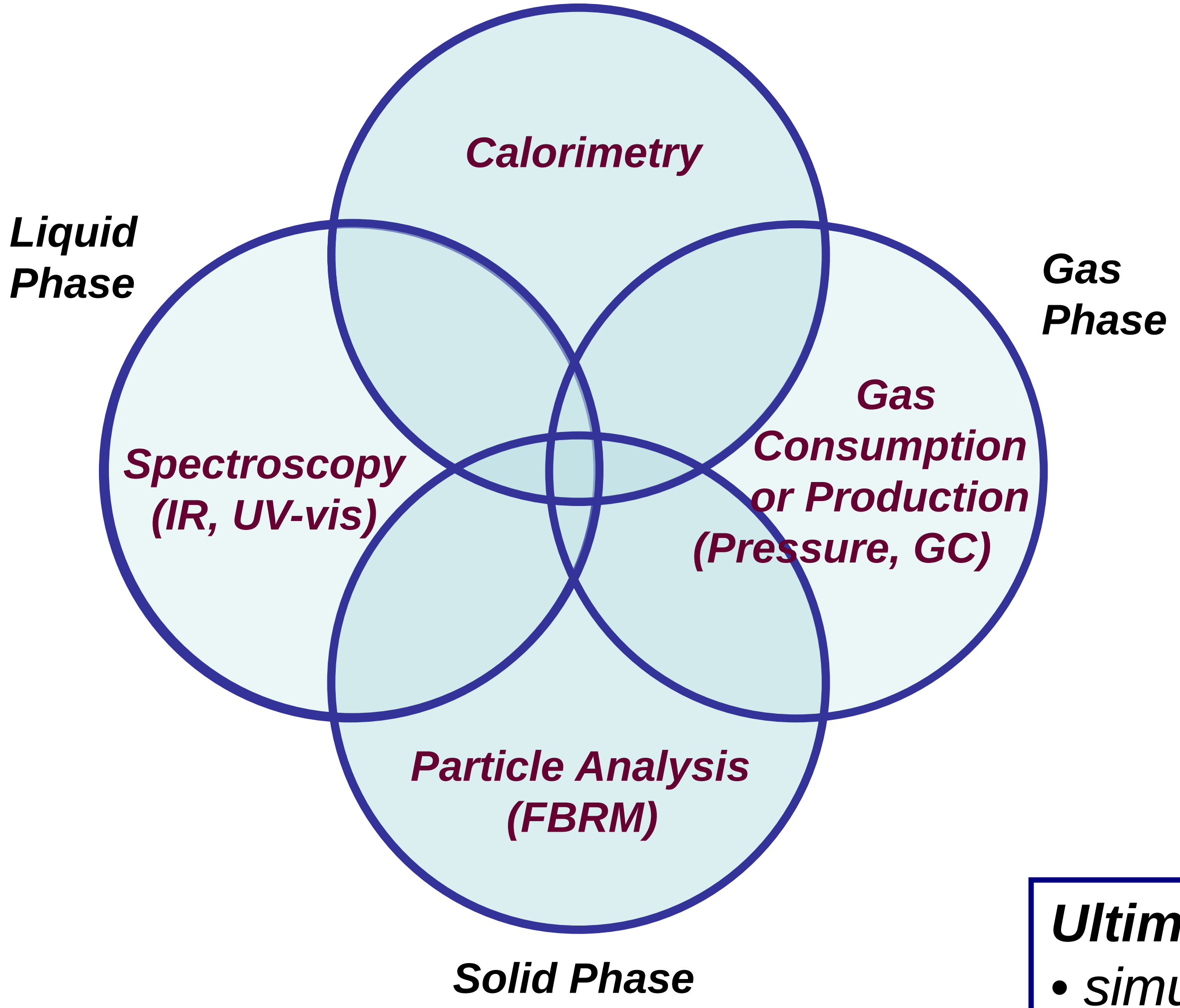
Specifications

- 25 to 50 ml
- -30°C to 180°C (-60°C in constr.)
- 60 bar
- Heat transfer calibration free
- Max reaction power 3 kW/L
- ATR probe integrated into the bottom of the reactor vessel
- Multiple free 6.5 mm inlets (8mm inlet in constr.)
- Interchangeable reactor vessel
- Parallelization possible
- Visualisation with endoscope

Accuracy

- Max. temp. dev. ≈ 0.5 °C/kW/L
- Detection limit ≈ 2 W/L
- Time constant:
  - Comp. heater = 4 s
  - Peltier = 15 s

Applications



On-line monitoring of reactions by multiple in-situ analytical devices

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Reaction mechanism, rate/equilibr. constants, reaction enthalpies, pure species spectra

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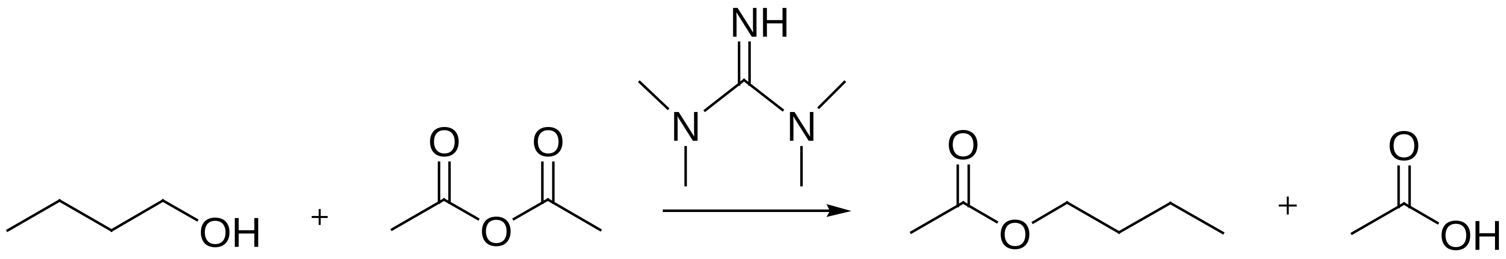
Ultimate goal:

- *simultaneous analysis of all signals*

Solvent Free Butanol Esterification

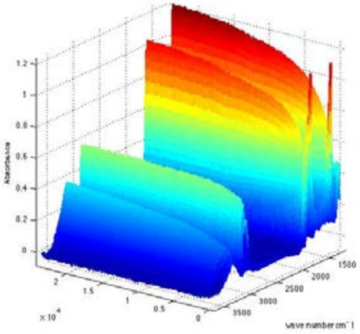


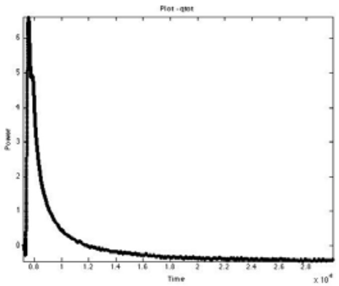
1,1,3,3-tetraethylguanidine

1-Butanol (BuOH)	Acetic anhydride (AA)	(TMG)	butyl acetate (BuOA)	acetic acid (AH)

n_{BuOH}:n_{AA} / moles	Temp. (°C)	c_{TMG} / M
1:1	40	0.4

Mid-IR spectra measured simultanously to **calorimetry**





- Puxty et al, **2006**, *Chimia*, 60, pp. 605-610
- Puxty et al, **2007**, *Chem. Eng. Sc.*, Submitted

Data Analysis

Soft-modelling methods:

- Principle component analysis
- Alternating least-squares with constraints
- Evolving factor analysis

Hard-modelling methods:

- Fitting of physico-chemical model using nonlinear regression:
  - Newton-Gauss-Levenberg/Marquardt method
  - genetic algorithms
- Fitting of models to:
  - spectroscopic data
  - calorimetry data
  - gas consumption data

Hard Modelling

Model

$$\upsilon = k \cdot c_{\mathrm{BuOH}} \cdot c_{\mathrm{AA}} \cdot c_{\mathrm{TMG}}$$

$$\frac{dc_{\mathrm{BuOH}}}{dt} = -\upsilon + \frac{f_{in}}{V} \cdot (c_{in,\mathrm{BuOH}} - c_{\mathrm{BuOH}})$$

$$\frac{dc_{\mathrm{AA}}}{dt} = -\upsilon - \frac{f_{in}}{V} \cdot c_{\mathrm{AA}}$$

$$\frac{dc_{\mathrm{BuOA}}}{dt} = \upsilon - \frac{f_{in}}{V} \cdot c_{\mathrm{BuOA}}$$

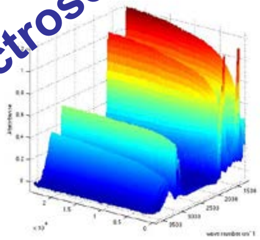
$$\frac{dc_{\mathrm{AH}}}{dt} = \upsilon - \frac{f_{in}}{V} \cdot c_{\mathrm{AH}}$$

$$\frac{dc_{\mathrm{TMG}}}{dt} = -\frac{f_{in}}{V} \cdot c_{\mathrm{TMG}}$$

$$\frac{dV}{dt} = f_{in}$$

Spectroscopy

$$\mathbf{Y = C \times A + R}$$



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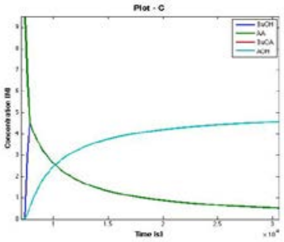

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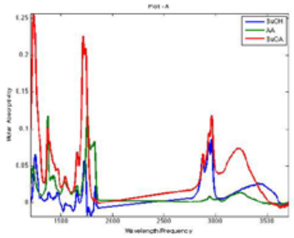

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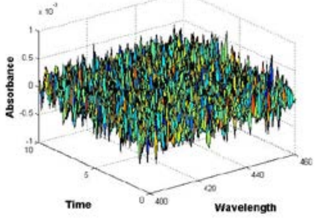
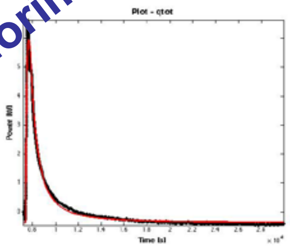


$$k_{40°\mathrm{C,IR}} = 1.7\times10^{-4}\ \mathrm{M^{-2}s^{-1}}$$

Calorimetry

$$\mathbf{q = N \times \Delta H + r}$$



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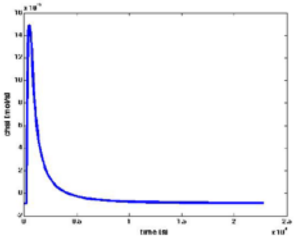

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$\Delta H = -40\ \mathrm{kJmol^{-1}}$

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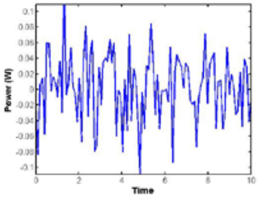
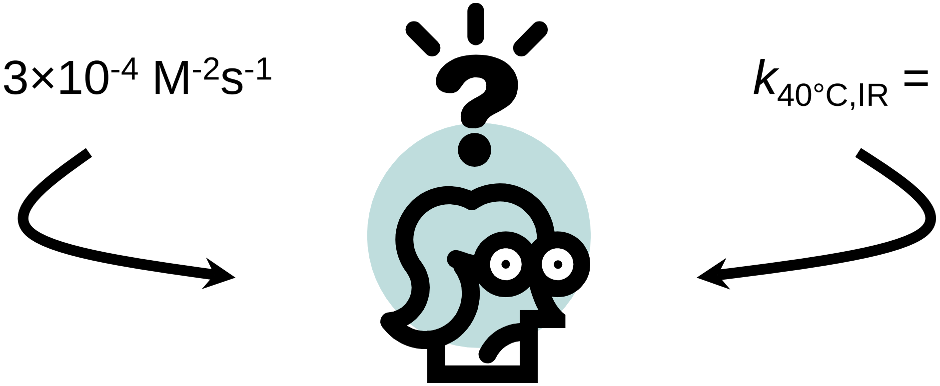


$$k_{40°\mathrm{C,calo}} = 5.3\times10^{-4}\ \mathrm{M^{-2}s^{-1}}$$

Data Analysis

$k_{40°\mathrm{C,calo}} = 5.3\times10^{-4}\ \mathrm{M^{-2}s^{-1}}$



$k_{40°\mathrm{C,IR}} = 1.7\times10^{-4}\ \mathrm{M^{-2}s^{-1}}$

What data do you trust more?

What is the ´**best**´ **compromise** when optimising **calorimetric** and **spectroscopic** signals simultaneously?

Residuals between spectroscopic signals and model	$\mathbf{R} = \mathbf{Y} - \mathbf{C} \times \mathbf{A}$	➔	$\mathbf{ssq_{spec}}$
Residuals between calorimetry signals and model	$\mathbf{r} = \mathbf{q} - \mathbf{N} \times \mathbf{\Delta H}$	➔	$\mathbf{ssq_{cal}}$

Conclusions

- Development of small scale reaction calorimeters
  - with in-situ IR-, UV-vis spectroscopy, gas consumption/production, on-line micro GC* & particle analysis*
- Elucidation of reaction mechanisms
  - reaction enthalpies, rate constants, activation energies
  - to achieve/maintain efficient and safe reaction conditions
- Development of algorithms/tools
  - multivariate kinetic modelling of the various signals

** in project*

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