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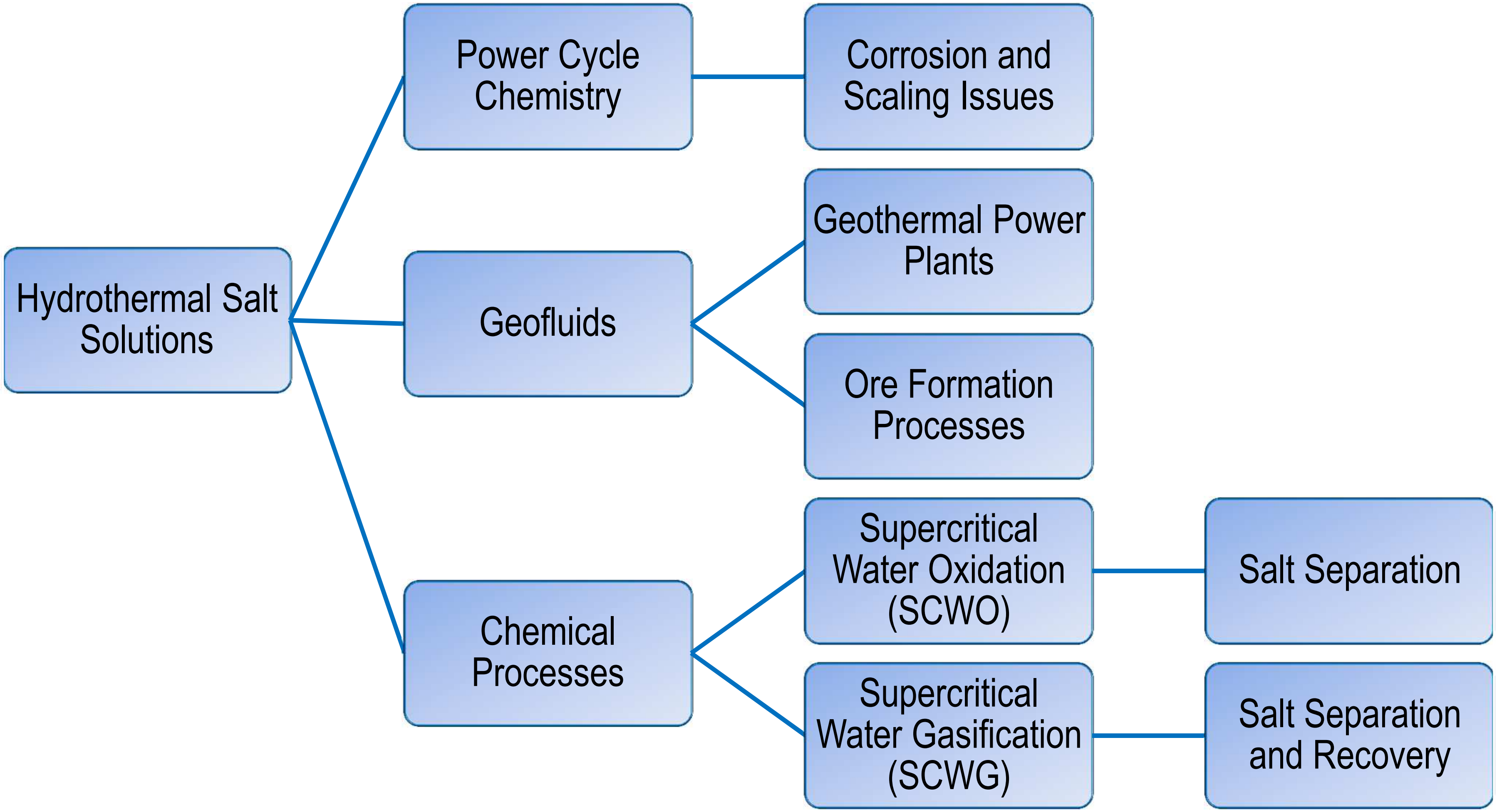
Wir schaffen Wissen – heute für morgen

Paul Scherrer Institut

Joachim Reimer

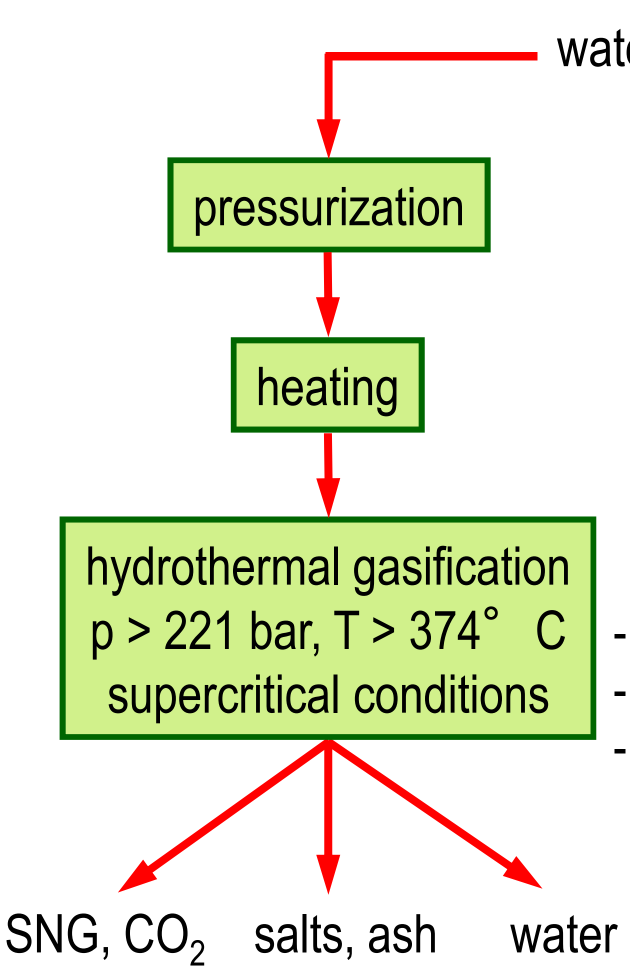
Biomass related Salt Solutions at Hydrothermal Conditions

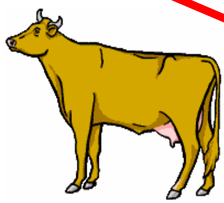
Introduction – Salt solutions at elevated p and T



Background – Gasification of Wet Biomass

Continuous salt separation is part of the PSI process of hydrothermal gasification of wet biomass to synthetic natural gas (SNG) in supercritical water.



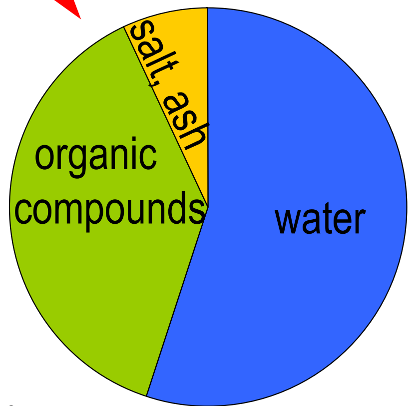


manure

sewage sludge*

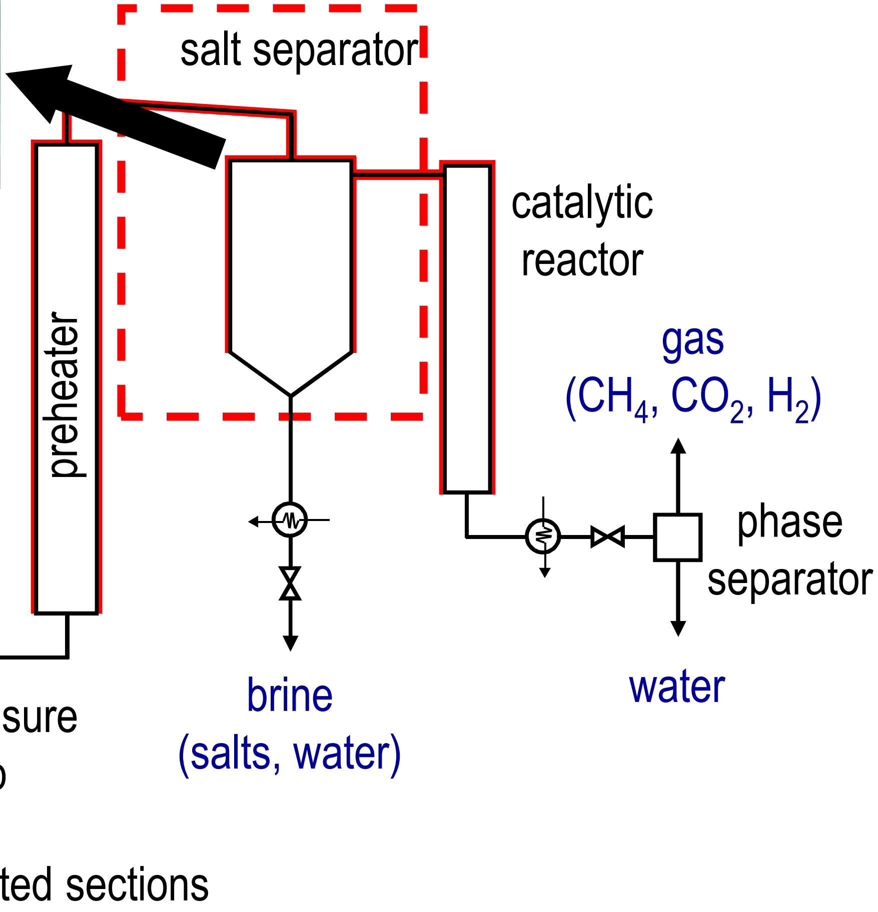
other organic waste streams

Why SCW?
- avoid evaporation of water
- good solubility for tarry compounds
- reduced solubility for salts



*http://www.sagen.at/fotos/showphoto.php/photo/6310

PSI Hydrothermal Gasification Process

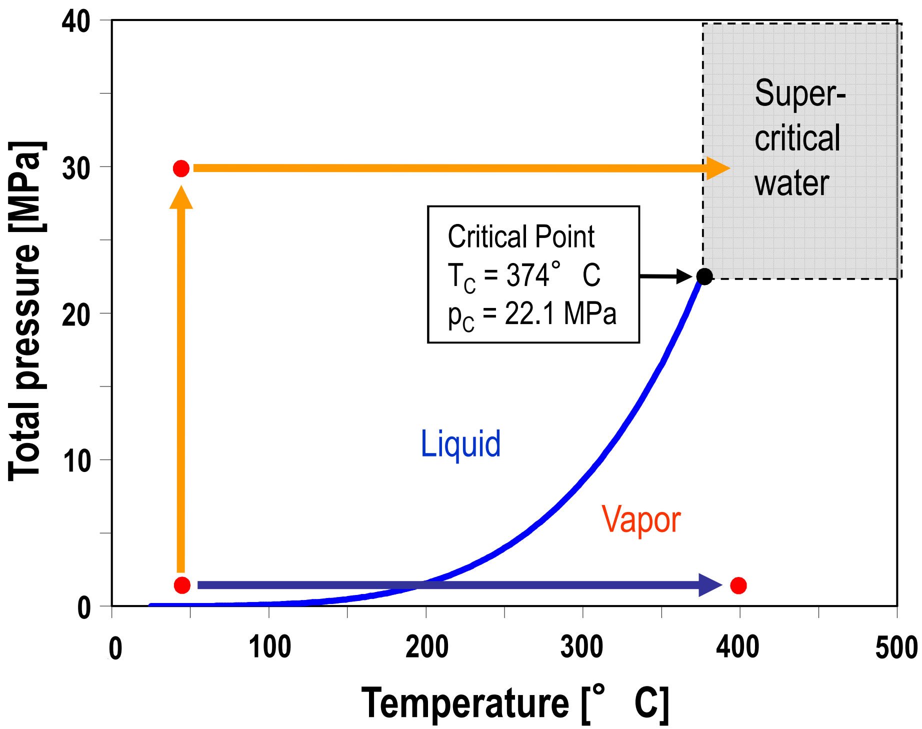


Challenges:

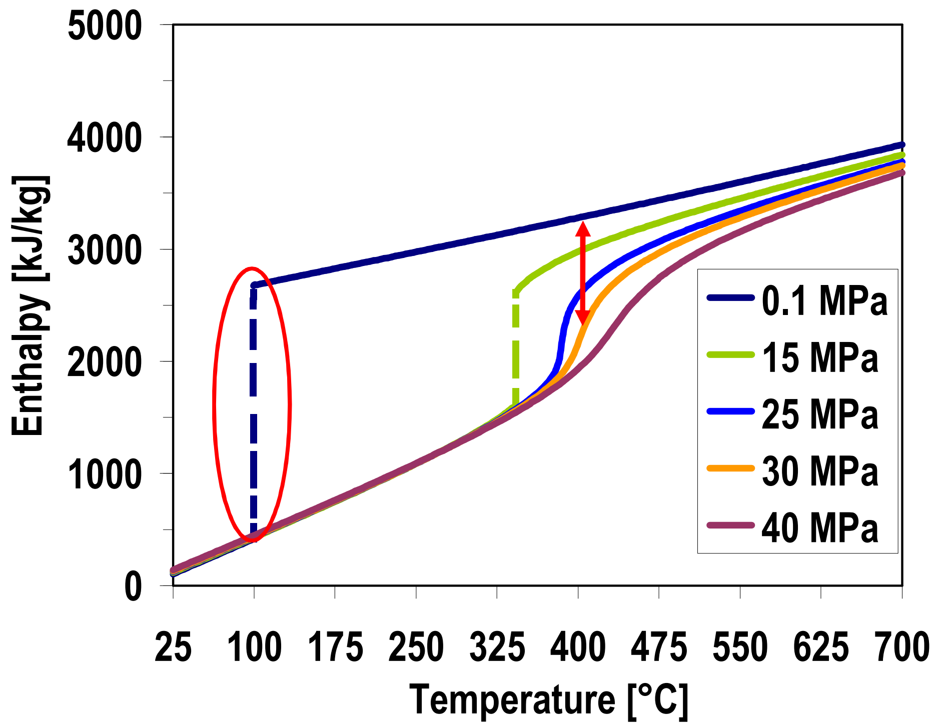
- precipitation of solid salt leads to blocking of the apparatus
- sulfur species poison the methanation catalyst
- phosphorus and potassium are valuable components, which could be re-used as fertilizer in biomass production

An effective salt separation and recovery is the crucial issue in the hydrothermal gasification process!

Introduction – Properties of Water at elevated p and T



Source: NIST Chemistry Webbook



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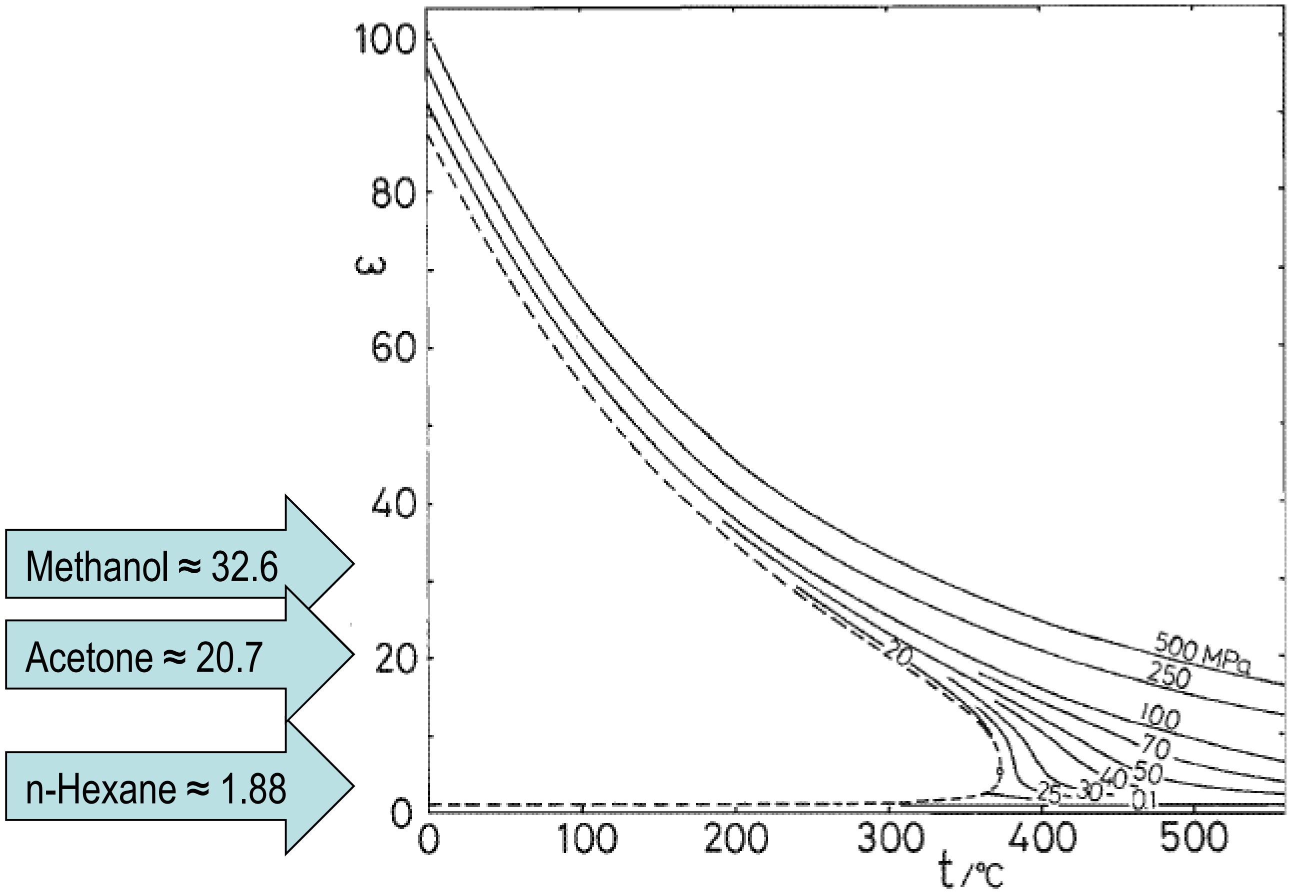
Introduction – Properties of Water at elevated p and T



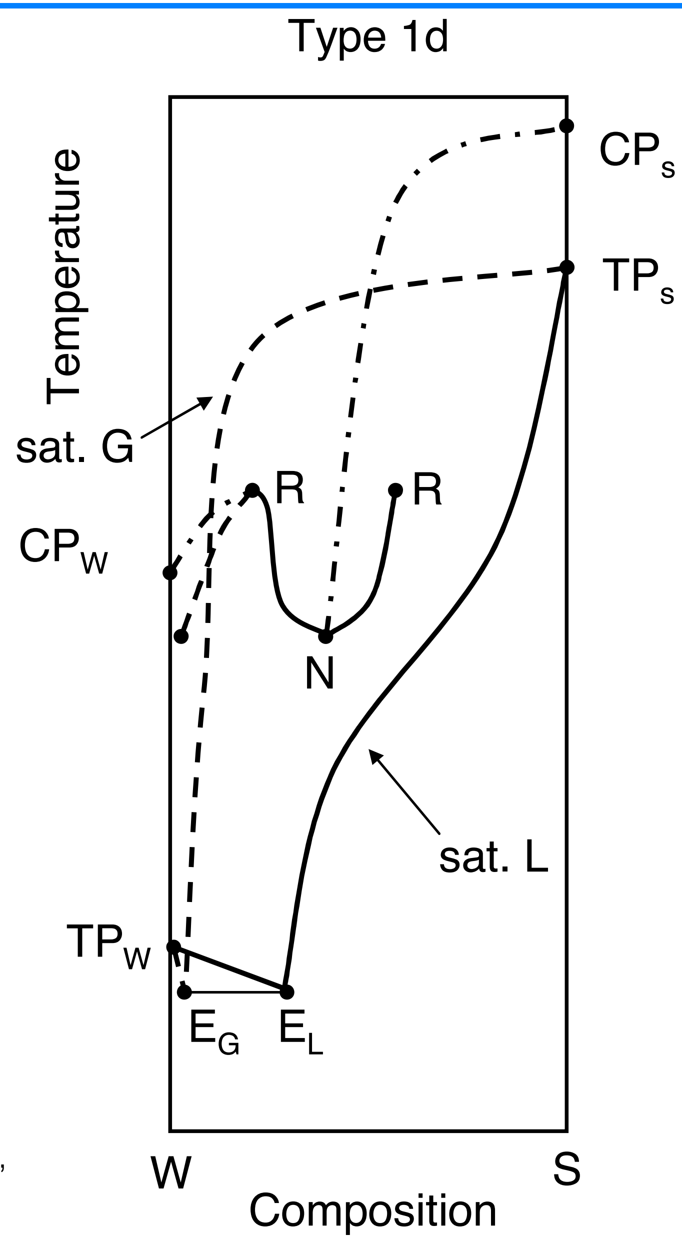
- The dielectric constant of water becomes similar to those of typical organic solvents at high pressures and temperatures.
- Increased solubility of organic substances

Taken from M.Uematsu & E.U. Franck, J. Chem. Phys. Ref. Data, Vol. 9, No. 4, 1980.

Phase diagrams of typical salt solutions – Type 1d

Type 1d:

- Continuous solubility line (G-L-S) from triple point of water to triple point of salt
- Liquid immiscibility starts at lower critical point N
- At upper critical point R the dilute liquid solution and the gas phase become equal
- Solutions Na_2HPO_4-H_2O, K_2HPO_4-H_2O

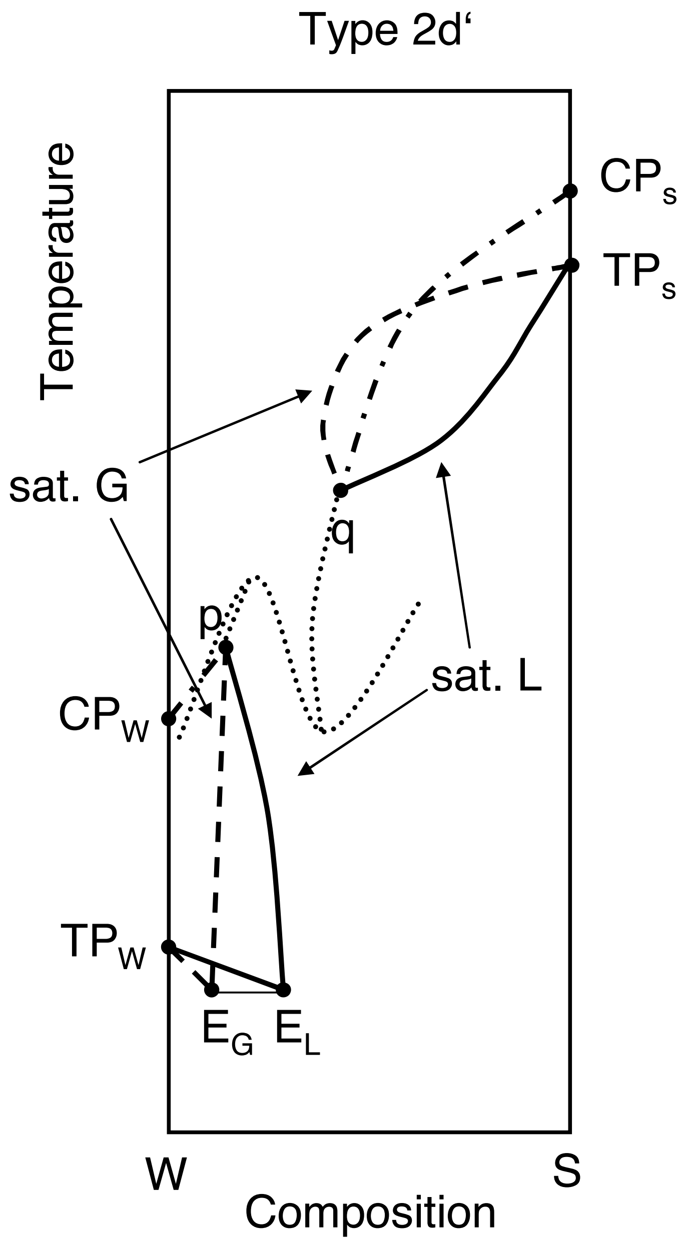


Adapted from: V. M. Valyashko, Phase equilibria in binary and ternary hydrothermal systems, in Hydrothermal Experimental Data, pages 1–133, John Wiley & Sons, Ltd, 2008.

Phase diagrams of typical salt solutions – Type 2d’

Type 2d’:

- Discontinuous solubility line (G-L-S)
- Intersection of solubility line (G-L-S) with vapor-liquid critical line in the lower critical end point p respectively in the upper critical end point q.
- Between p and q either a one phase fluid or a fluid in equilibrium with solid exists.
- Metastable liquid immiscibility which ‘bridges’ the gap between the critical endpoints p and q
- Solutions Na_2SO_4-H_2O, K_2SO_4-H_2O



Adapted from: V. M. Valyashko, Phase equilibria in binary and ternary hydrothermal systems, in Hydrothermal Experimental Data, pages 1–133, John Wiley & Sons, Ltd, 2008.

DSC-Measurements - Instrumentation

- Setaram Sensys DSC with Calvet-sensor

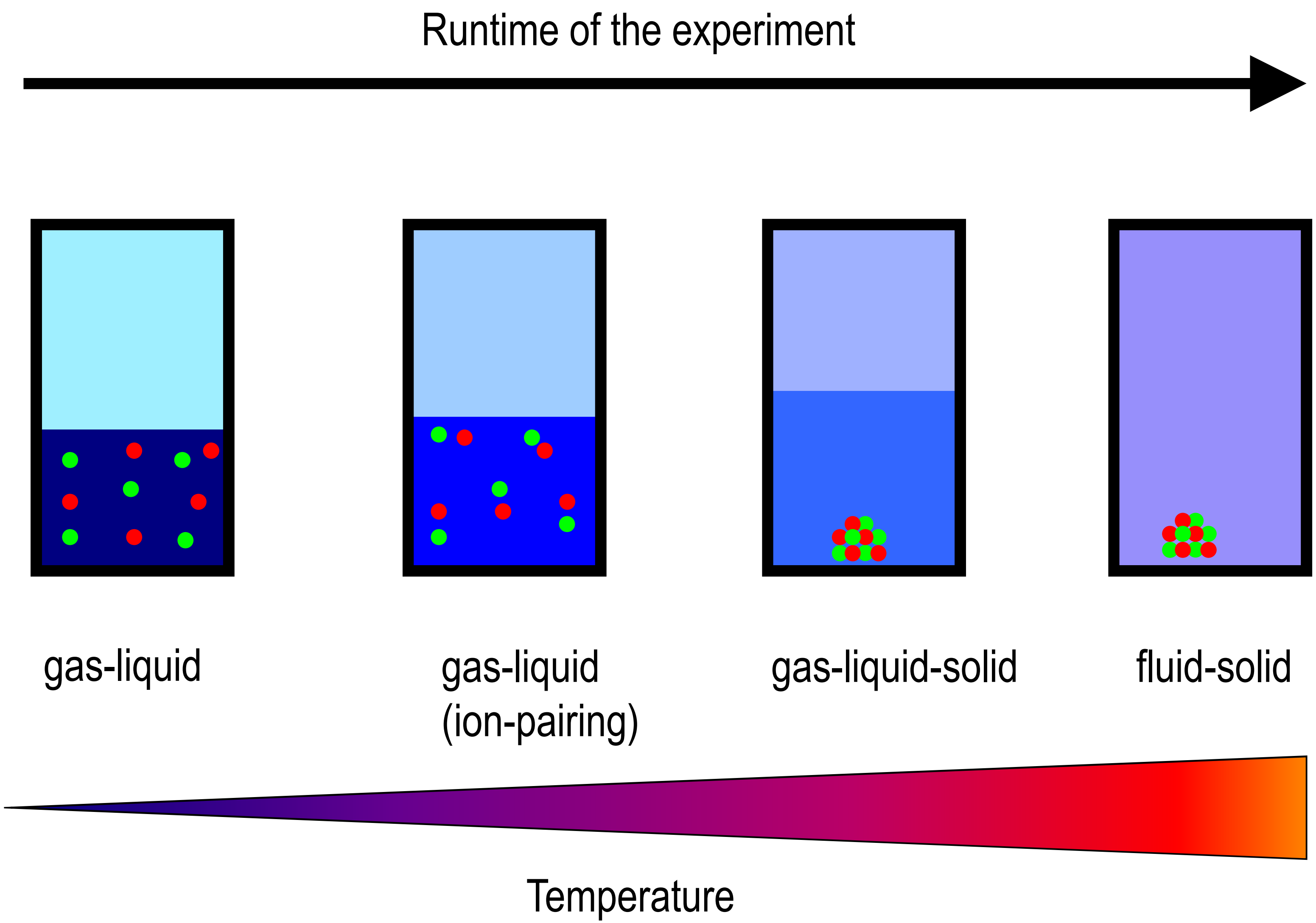
- Incoloy®-crucibles suitable up to 600° C/500 bar

- nominal inner volume: 130 µL
- volume as determined: 128.63 µL

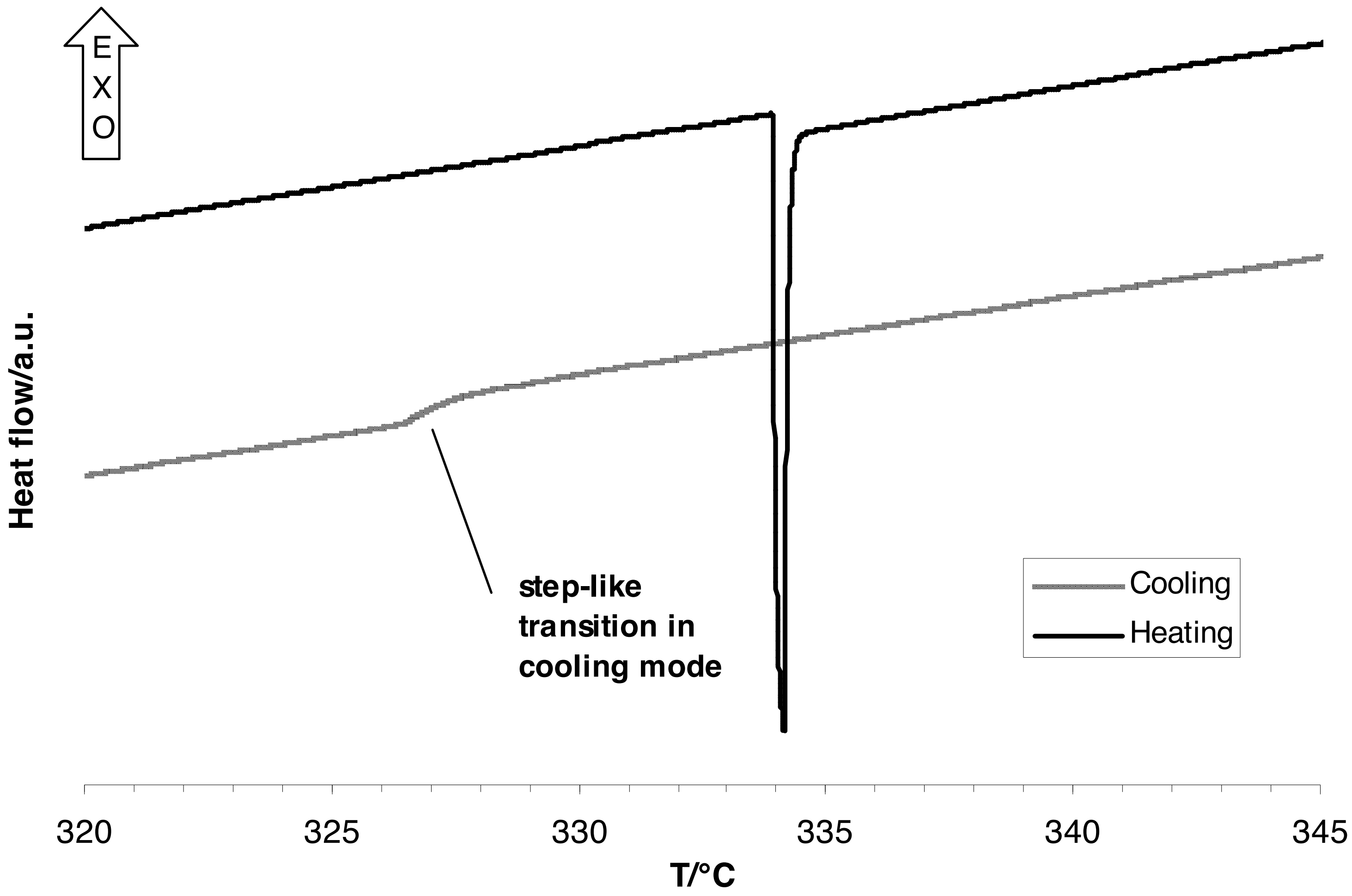
- heating rate 0.1 K/min or 0.05 K/min
- carrier gas 20 mL/min Argon
- measurement interval 300-400° C

- 3 cycles with 1h stabilization period prior to measurement
- sample weight: 38.6 mg corresponding to 300 kg/m^3 overall density

DSC-crucible during measurement

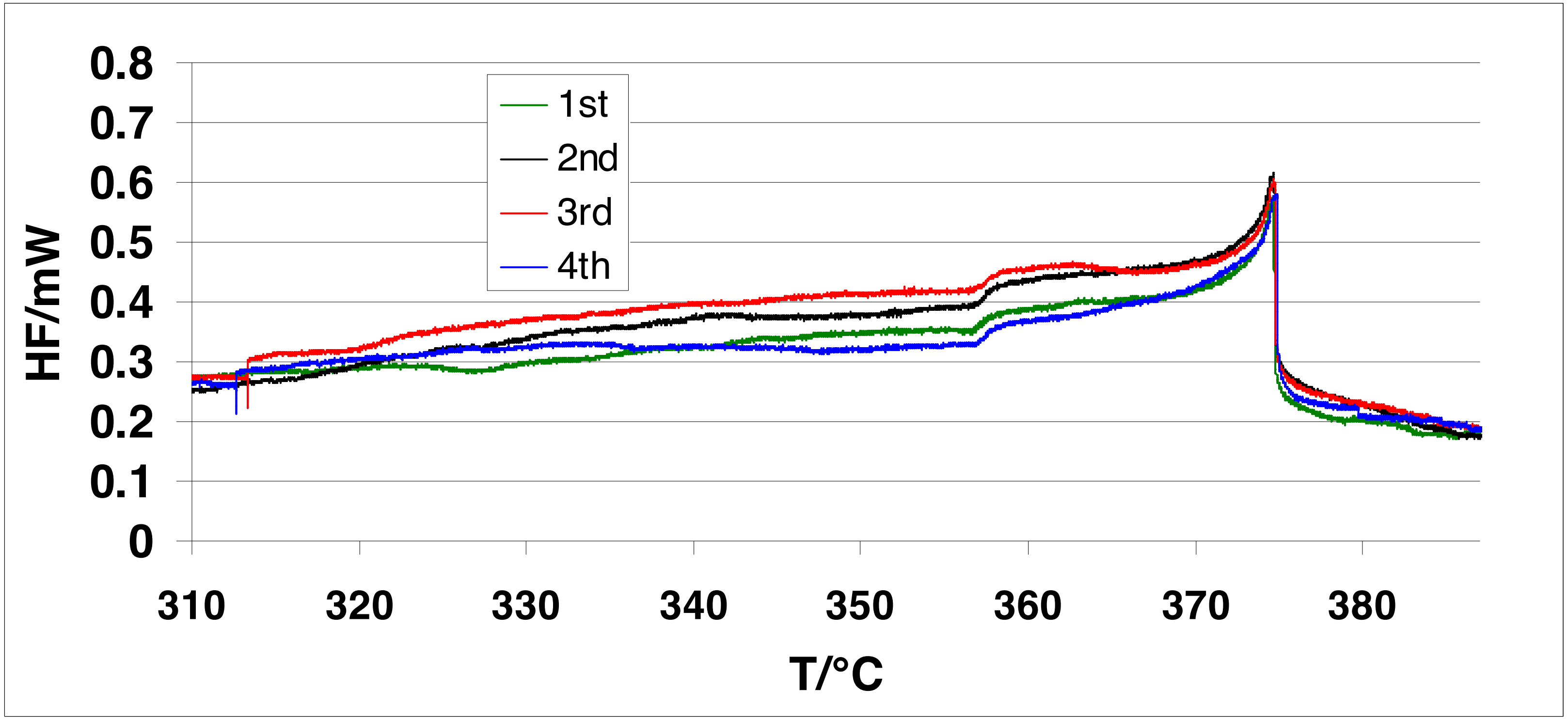


DSC-Measurements – Heat flow curves



J.Reimer, F.Vogel, RSC Adv., 2013,3, 24503-24508.

Heat flow curves in the cooling mode



- Limited to small sample mass (mg range) therefore small signals at low heating/cooling rates

$$\Phi_{measured} = \Phi_{sample} + \Phi_{baseline} = c_V \cdot m \cdot \beta + \Phi_{baseline}$$

- High deviations in heat flow curves and measured baselines → big error in C_V
- Error in onset-temperatures of the phase transitions on repetition is smaller than 0.3° C

DSC-Measurements – correction of the data points

$$\rho_{vap}V_{vap} + \rho_{liq}\left(V - V_{vap}\right) = M \qquad \Leftrightarrow \qquad (1)$$

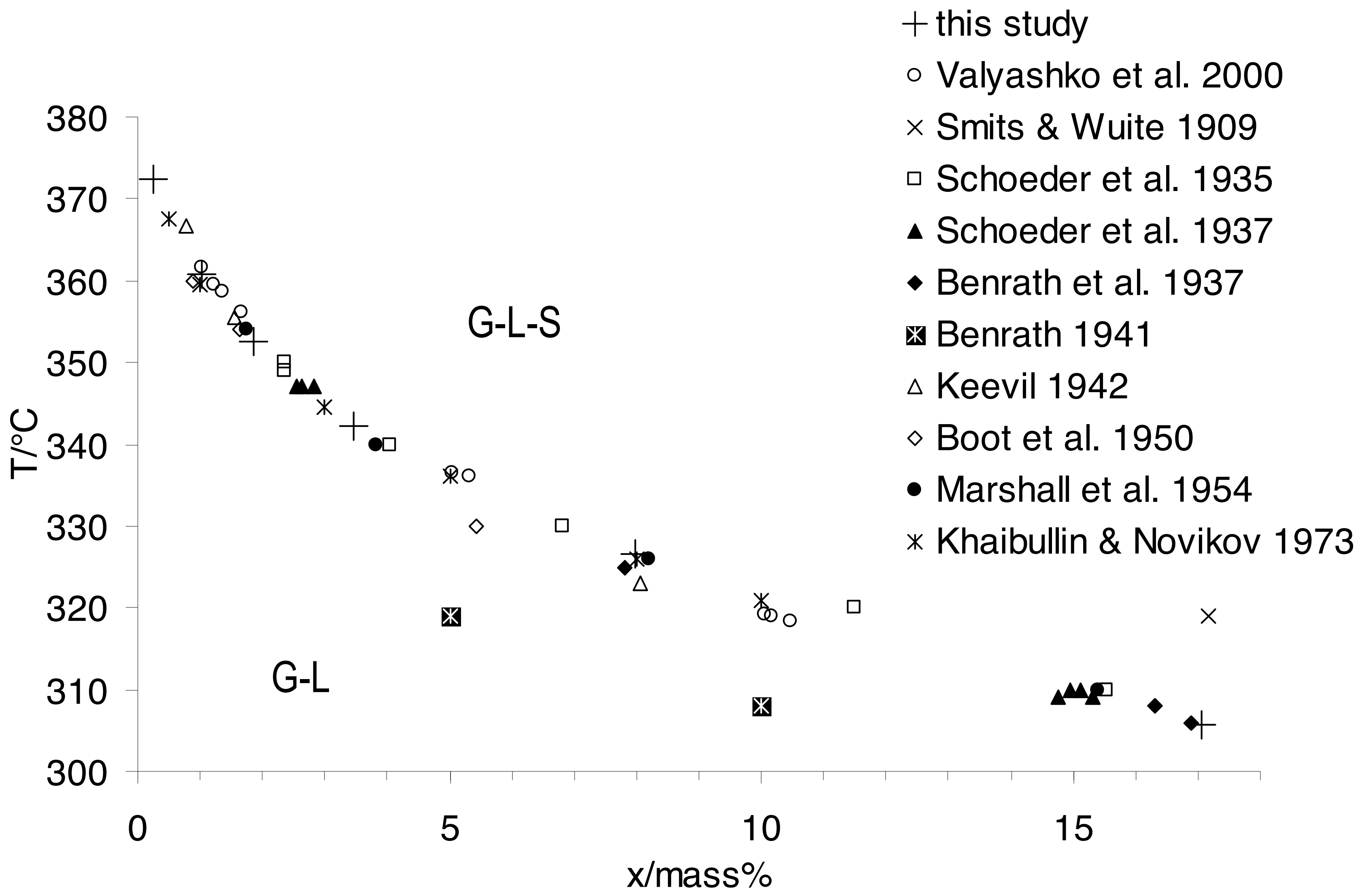
Density data from literature needed!

$$V_{vap} = \frac{\rho_{liq}V - M}{\rho_{liq} - \rho_{vap}} \qquad (2)$$

$$\frac{x_{liq}}{100\ wt.\%} = \frac{M_{salt}}{\rho_{liq}V_{liq}} = \frac{M_{salt}}{\rho_{liq}\left(V - V_{vap}\right)} \qquad (3)$$

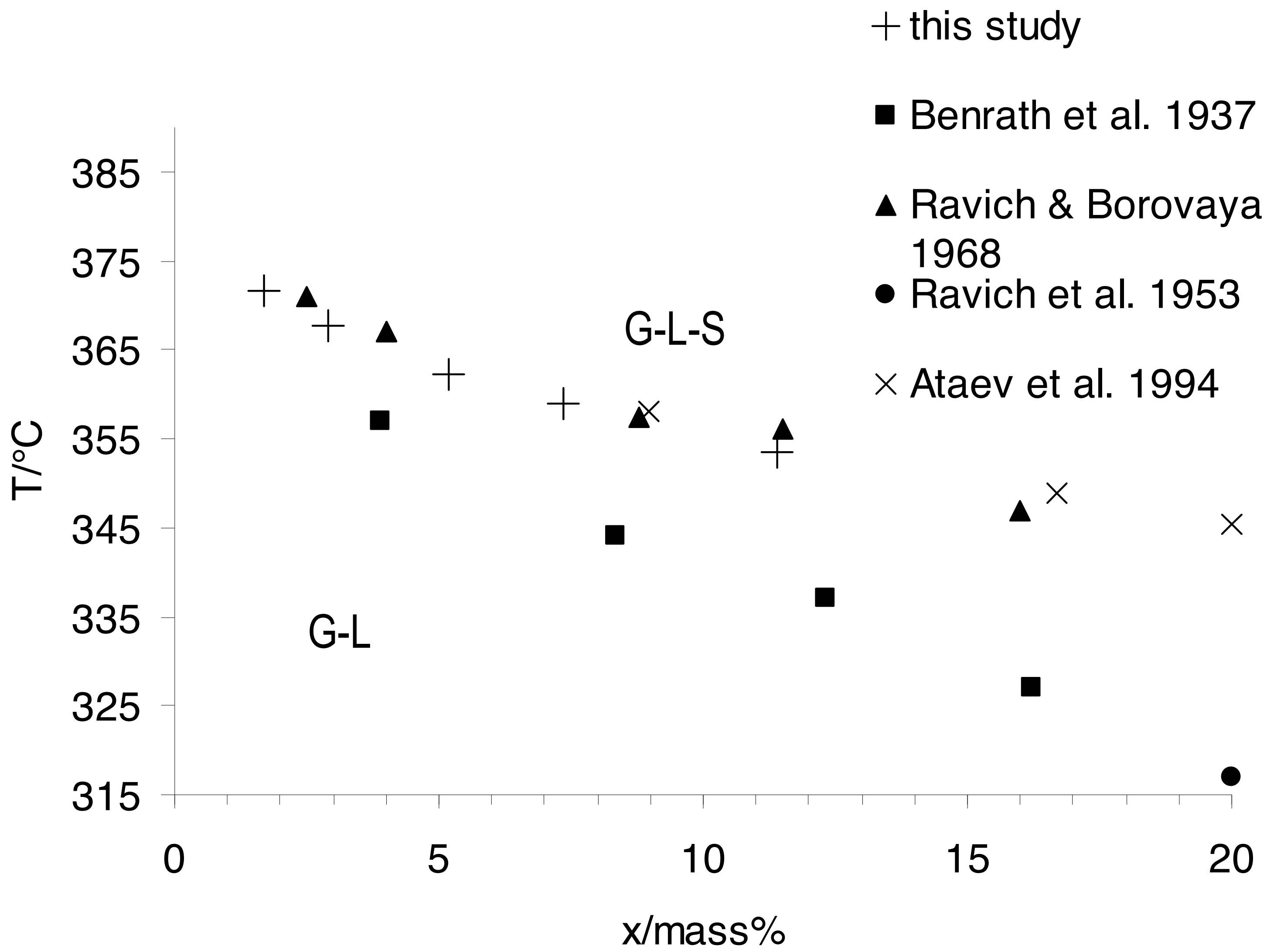
Adapted from: Valyashko *et al.*, J. Chem. Eng. Data, **2000**, *45*, 1139-1149.

DSC-Measurements – Results Na_2SO_4



J.Reimer, F.Vogel, RSC Adv., 2013,3, 24503-24508.

DSC-Measurements – Results K_2SO_4



J.Reimer, F.Vogel, RSC Adv., 2013,3, 24503-24508.

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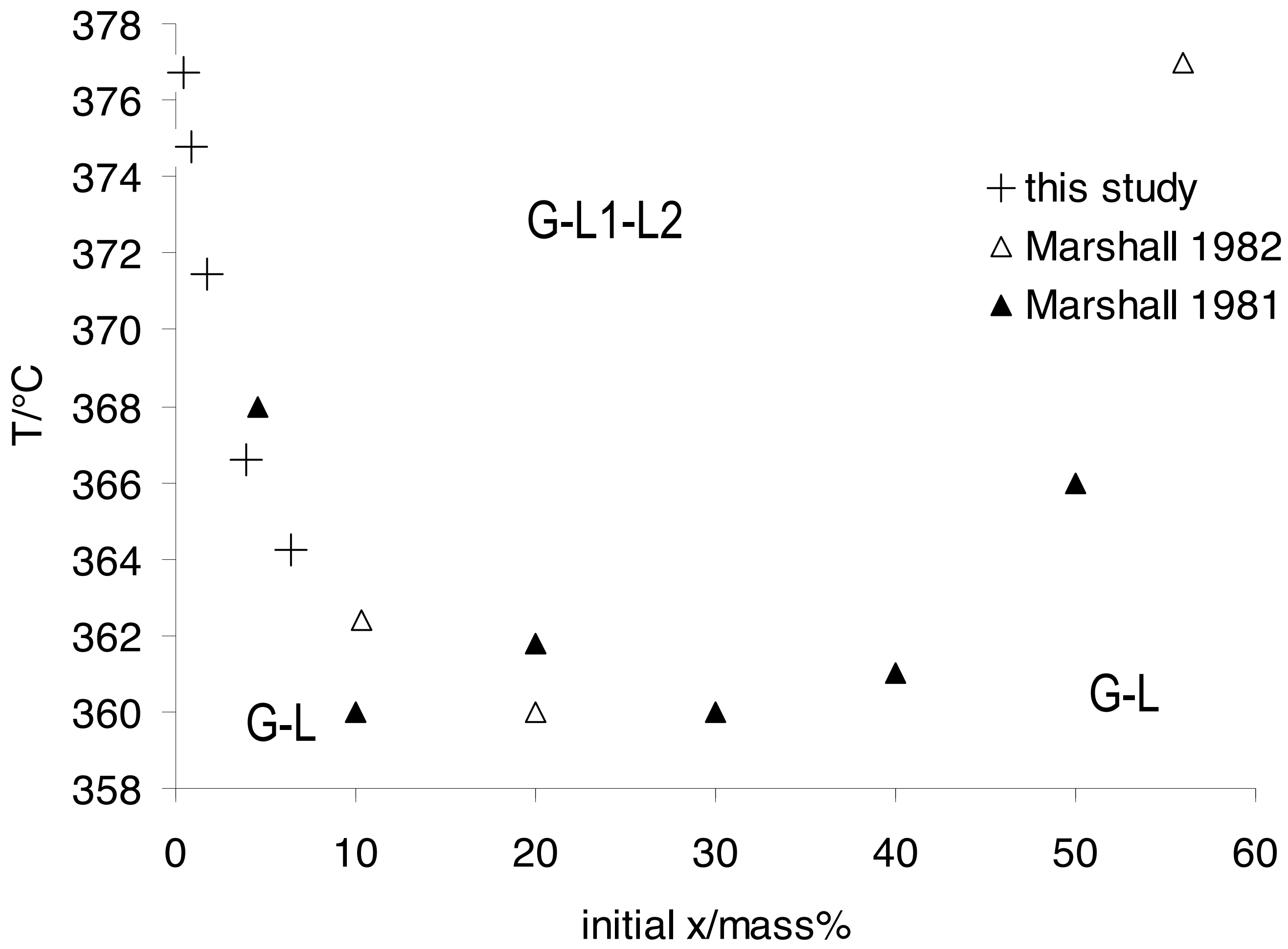
DSC-Measurements – Results K_2HPO_4



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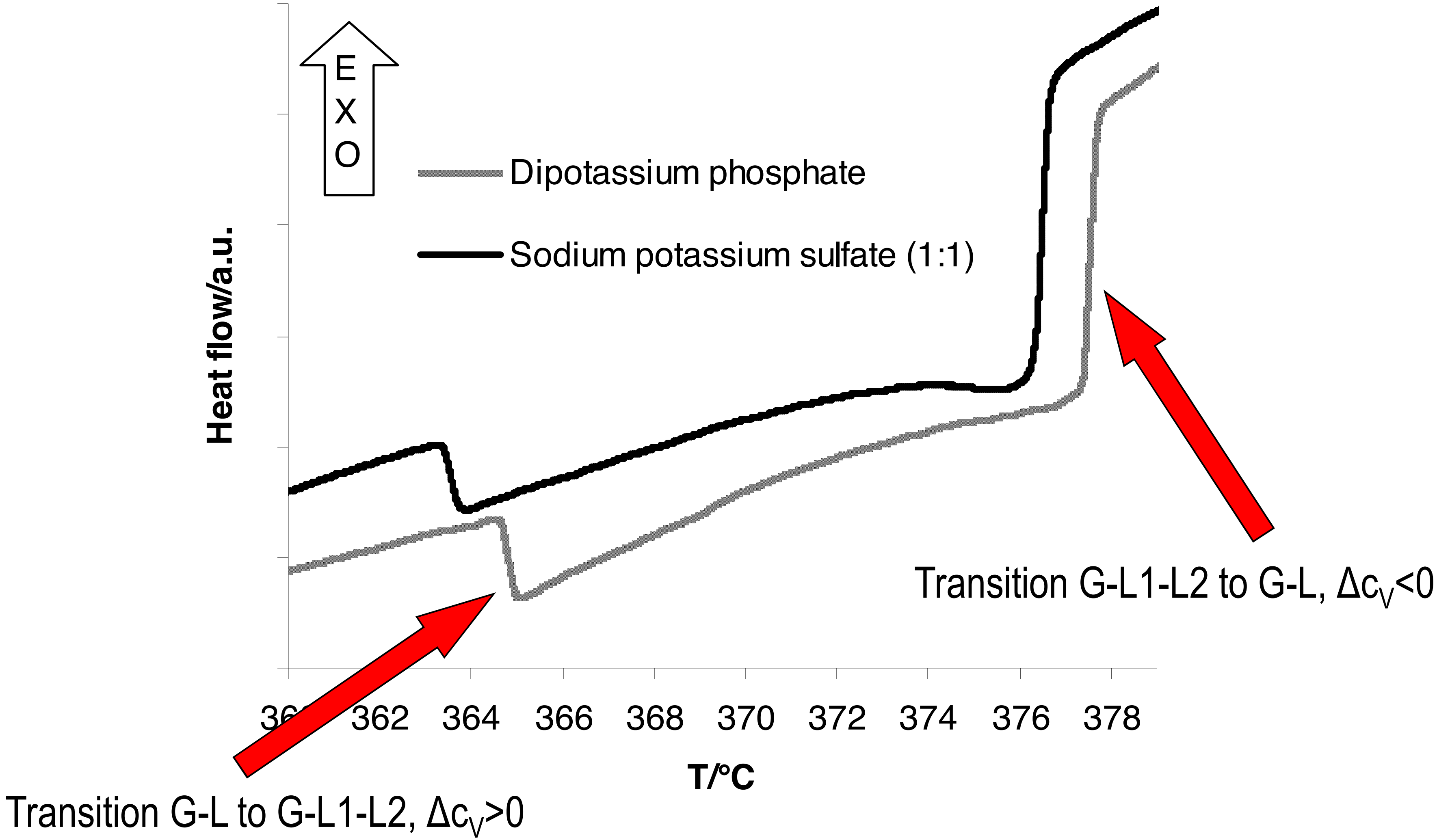
Comparison K_2HPO_4-H_2O and Na_2SO_4 -K_2SO_4-H_2O



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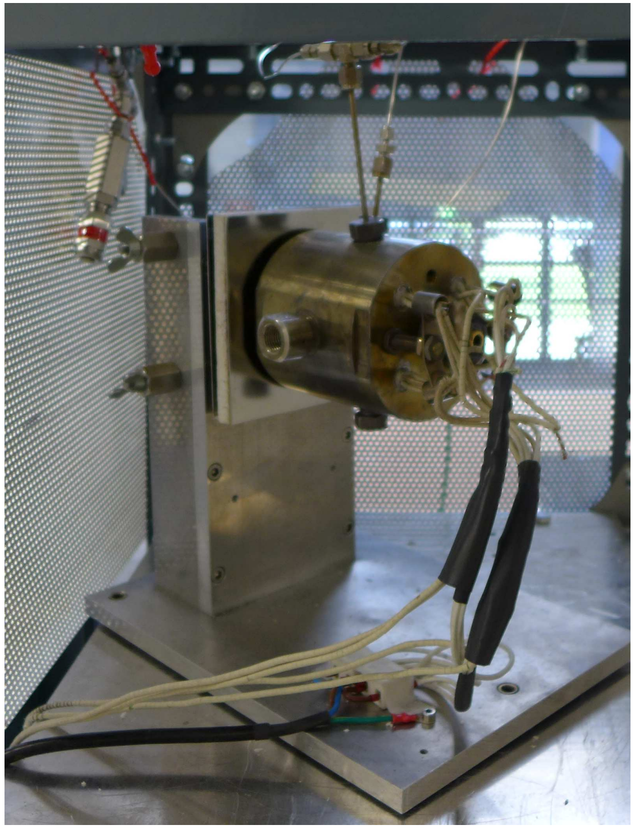
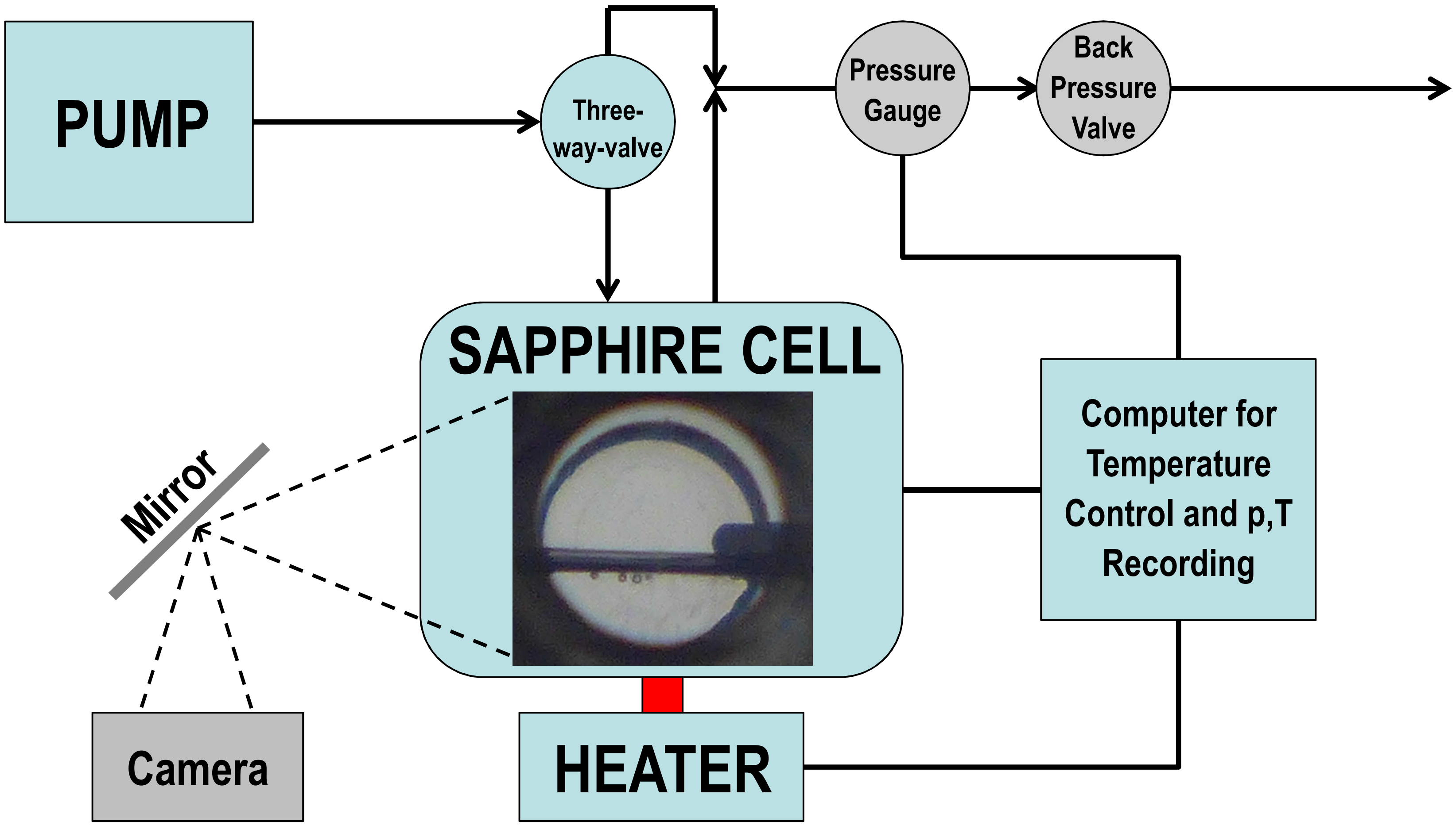
The Sapphire Cell

- A high temperature and pressure cell that allows the phase behaviour of salt solutions to be visually observed.



The Sapphire Cell



Summary…

- DSC is a good tool to investigate phase transitions qualitatively and if phase density data is available also quantitatively.
- Corresponding vapor pressures need to be measured separately.
- Higher mixtures of salts can exhibit a totally different phase behavior compared to binary mixtures.
- The measured data yields a deeper insight into the salt separation process and offers the opportunity to improve the salt separation.

Many thanks to …

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