

Reaction calorimetry in new dimensions

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Investigation into the suitability of HFC (Heat Flow Calorimetry) and HBC (Heat Balance Calorimetry) in non-isothermal, homogeneous and inhomogeneous 1- and 2-phase systems (liquid/solid)

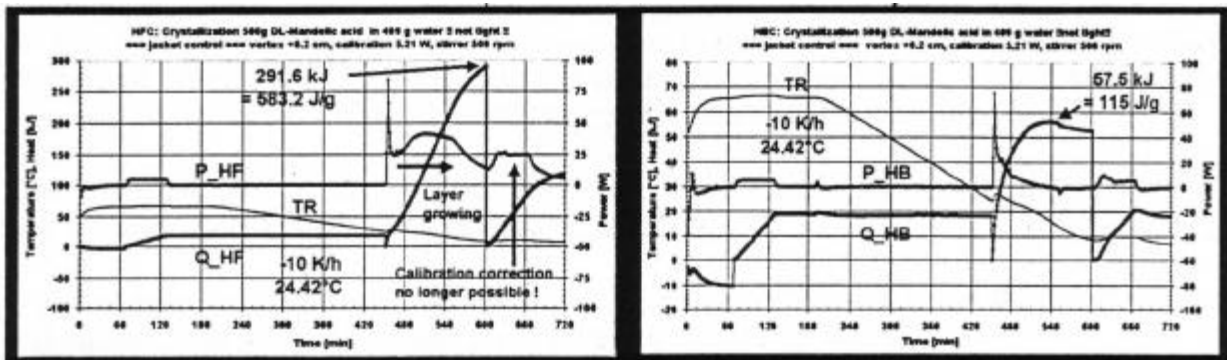
During non-isothermal investigations with conventional heat flow calorimeters problems occur with base line stability, especially in a 2-phase system (liquid/solid). Most difficulties occur with inhomogeneous 2-phase systems. The transition from homogeneous to inhomogeneous is gradual and until today it was extremely difficult to give some information about credibility of measured results.

With DL-Mandelic acid as an example, we can show all influences in a 1- and 2-phase (liquid/solid) homogeneous and inhomogeneous system. All investigations were made in the new SYSTAG Calo 2100 reaction calorimeter which measures simultaneous heat flow and heat balance.

The accurate base line (directly calibrated in Watts) shows the new capabilities of a real non-isothermal calorimeter for both HF and HB measurements.

The additional heat balance calorimetry is a very robust and also sensitive method. With this a verification of the experimental results is finally possible. Both non-isothermal methods (HFC & HBC) allow very accurate kinetics in homogeneous systems, in inhomogeneous systems, the heat balance method is the only one with acceptable results.

Example: 50% DL-Mandelic acid, ramp 65°C - 5°C downwards, -10 K/h, jacket controlled



Heat flow calorimetry (HFC), run 08

Heat balance calorimetry (HBC), run 08

With jacket control (-10 K/h) we realised an extreme inhomogeneity! A thick layer was built up after the spontaneous crystallisation. This leads to a simulated power increase (P_HF) by the heat flow calorimetry (HFC left diagram). The right diagram (P_HB of HBC) shows clearly the expected real and normal behaviour. The HBC result of 115 J/g is larger than the mean value of 91 J/g but not as far away as the HFC result of 583.2 J/g. The remaining HBC measurement error is the result of a non ideal model for the inhomogeneous phase because the TR probe was near or already enclosed in the crystal layer.

References:

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- [3] L. Hub and T. Kupr, 'Heat balance calorimetry and automation of testing procedures', *Symposium runaway chemical reaction hazards*, IBC December 2/3 1987, London