

Determination of the measurement accuracy of reaction calorimetric investigations under difficult reaction conditions for the heat flow balance

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The determination of safety-related parameters with the help of reaction calorimetric investigations represents an important basis for the safe scale-up of chemical processes. The accuracy of reaction calorimetric measurements can be influenced by various parameters and lead to measurement tolerances. The aim of the tests carried out is to investigate the influences on the heat balance of the RC1e calorimeter caused by the viscosity of the reaction mixture, reactions with superimposed heating phases, as well as boiling effects occurring during a reaction process, which can be caused by the formation of low boilers. For the investigations, reaction mechanisms known from literature are used and the experiments are carried out under the influence of the described parameters. The results obtained are evaluated and analysed accordingly in order to determine the measurement tolerance of reaction calorimetric investigations under difficult reaction conditions for the heat flow balance.

The tests carried out show that the reaction calorimetry is significantly influenced from viscosities of 500 mPa·s and that no reliable results can be obtained from viscosities of 16600 mPa·s in RC1e. Superimposed heating ramps with a final temperature at least 50 K below the boiling point of the reaction mixture give a slightly conservative result. Heating ramps that end above the boiling temperature of the reaction mixture cannot be investigated by reaction calorimetry, even with pressurisation to suppress the boiling effects that set in. For reactions with constant reflux conditions, a too low reaction enthalpy is determined. Based on the series of experiments carried out on reactions with initiating reflux, several methods have been worked out that can be used to measure these reaction systems.