

# Pitfalls in Calorimetry

Francis Stoessel

Swissi Process Safety GmbH, Mattenstrasse 24a, CH-4058 Basel

Reaction calorimetry is presently a well-established calorimetry technique. It is widely spread as well in process research and development laboratories as in safety laboratories. Even if in most commercial calorimeters, the instrument software allows for practically automatic evaluation of the experiments, it does not mean that errors are avoided. Some examples of common errors are shown in the presentation.

When semi-batch reactions are studied, the continuous addition of at least one reactant results in a reaction mass that varies with time. This renders the evaluation of some parameters difficult and may be the cause of errors.

As a first example, the question of what is the “right” power (heat release rate) of the reaction to be used for scale-up is not just straight forward. In the reaction calorimeter, one may determine either the absolute power, i.e. the power directly as measured or the specific power, i.e. the power expressed in W/kg of actual reaction mass. Generally the thermal power of a reaction is used to compare with the cooling capacity of an industrial reactor. Since in the industrial reactor the power also may vary with mass due to the increasing heat exchange area, the specific power is probably best suited for this task.

The changing mass also has consequences on the calculation of the Maximum Temperature of the Synthesis Reaction (MTSR): For a single bimolecular reaction, the maximum accumulation is reached at the stoichiometric point. But at this instant, the reaction mass is not yet complete, and the missing heat capacity may lead to an erroneous MTSR.

In the semi-batch reactor, the effect of the sensible heat due to the temperature difference between the reaction mass and the feed, may lead to an erroneous calculation of the conversion and consequently of the accumulation and MTSR.

Often reactions are more complex, and a frequently encountered reaction scheme is consecutive reactions with a first fast step, followed by a slow step. With those reactions, the accumulation is not due to unreacted reactant B (added reactant), but to the accumulation of an intermediate. In such cases the calculation of the MTSR may be significantly affected.

Examples will also be shown, how the calculation of gas pressures or volumes may be affected by the experimental conditions. Since the relationship between pressure and temperature is essential in the design of emergency pressure relief systems, the measurement and its interpretation must be done with care.