PARAMETERS INFLUENCING CORRECT PREDICTION OF AUTOCATALYTIC REACTIONS

Roduit Bertrand[1], Marco Hartmann[1], Folly Patrick [2], Sarbach Alexandre[2], Burelbach James[3]

[1]AKTS AG, http://www.akts.com, TECHNOArk 1, 3960 Siders, Switzerland, b.roduit@akts.com
[2]armasuisse, Science and Technology Centre, 3602 Thun, Switzerland
[3]Fauske & Associates, LLC, 16W070 83rd Street, Burr Ridge, Illinois 60527, USA

During simulation of the reaction progress α of autocatalytic reactions (characterized by a long induction period under isothermal conditions), not only the values of the kinetic triplet A, E and $f(\alpha)$ but also the "thermal history" of the sample has to be taken into consideration. Even very small (much lower than 0.01%) initial reaction progress α_0 of the analyzed sample, if not introduced into calculations, can significantly influence the predictions. In the present study we will show that this generally underestimated issue of the improper choice of the α_0 value at the beginning of the reaction ($t_0=0$ second) results in very significant errors during prediction of the reaction course. Additionally we will show that the importance of the correct choice of α_0 value depends significantly on the reaction model, i.e. whether the reaction is of accelerating, sigmoidal or decelerating type. For decelerating type reactions the influence of α_0 on the predictions is negligible, for accelerating and some sigmoidal types it has minor impact, but for the autocatalytic type reactions (sigmoidal) the use of correct α_0 is of great importance. Therefore, during prediction of the reaction course at any temperature profile, one has to use a "kinetic quartet" in which the α_0 value is additionally inserted beside the commonly applied kinetic triplet containing the activation energy E, pre-exponential factor A, and form of the function $f(\alpha)$ dependent on the reaction mechanism. The numerical optimization of the kinetic quartet to obtain the best fit of the experimental results must be performed starting from the beginning of the experiment, not simply from the point at which the first visible reaction progress is detected via thermoanalytical signals. This is due to the fact that even a very small reaction extent, being significant for the prediction, occurs much below the experimentally detectable beginning of the reaction. The problem of correct prediction of the course of autocatalytic reactions is especially important for thermal safety evaluations. Even applying the absolutely correct kinetic triplet for these types of reactions, but using a wrong value for α_0, it is impossible to predict correctly such important key parameters as the Time to Maximum Rate under adiabatic conditions (TMR_{ad}) or the Self Accelerating Decomposition Temperature (SADT) for the transport or storage of dangerous chemicals.