Heat-/Pressure-Accumulation Test - Adiabatic Calorimetry for Assessing Process Safety Relevant Parameters such as ADT_{24h} and T_{exo}

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Process Safety has been, is and will be a key factor while planning and enduringly carrying out chemical reactions on an industrial scale. Besides the reaction kinetics, a crucial parameter for a safety assessment of a chemical reaction is the heat balance which includes the system's cooling capacity. The heat removal capacity is worse for industrial-scale reactors due to the high volume to surface ratio. Therefore, from a safety point of view and for assessing even high scale-up systems the worst case and adiabatic conditions are most often assumed to account for the high volume to surface ratio.

Assessment of the criticality of a synthesis reaction during a cooling failure scenario and a possible transition to a decomposition reaction and a thermal runaway, experiments and the determination of safety-relevant parameters is needed. One of those parameters is the temperature for safe handling, the T_{exo}, which indicates a temperature up to which a decomposition reaction does not occur or is still controllable. The T_{exo} and decomposition behaviour on industrial scale can be determined in the adiabatic heat-storage test and carried out according to the test setup, according to Grewer and Klais and VDI-Guideline 2263 Page 1. This setup consists of a pressure vessel with a volume of approximately 0.75 l. A Dewar vessel is placed in this autoclave. The Dewar vessel isolates its content thermally from its surroundings by a double-walled vacuum jacket with a reflective coating. The autoclave is closed, placed in an oven and heated. After a reaction starts in the vessel, the oven's temperature is regulated to follow the sample temperature and establish quasi-adiabatic conditions. Additionally, the pressure in the headspace is measured and recorded.

Such an adiabatic experiment yields the time-dependent temperature and pressure curve of the decomposition, which is converted in gas production- and heat production rates. From the heat production rate, the activation energy and, additionally, the self-accelerating decomposition temperature *SADT* (for monomers, the *SAPT* as polymerizing temperature) can be received according to the UN-Transportbook, UN-Test H.2. The SADT is an essential parameter for transport classifications.

From a process safety point of view, the most relevant parameter recieved from an adiabatic heat-/pressure accumulation test is the ADT_{24h} or adiabatic induction time 24 hours before the highest temperature-increasing rate (the runaway). Sometimes, this parameter is known as the time to maximum rate (*TMR*). Adding a safety margin of 10 K to the determined ADT_{24h}, the T_{exo} can be obtained. It is one of the most relevant safety parameters for assessing a sample's thermal stability and evaluating a safety concept for a process.

- UN-Transportbook:
  UN Recommendations on the Transport of Dangerous Goods: Manual of Tests and Criteria, Rev. 7 (2019) and UN-Model Regulations, Rev. 22 (2021)
- Report of the Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals on its tenth session held in Geneva on 11 December 2020, Annex II: Amendments to the 7th revised edition of the Manual of Tests and Criteria (ST/SG/AC.10/11/Rev.7) (2020/2021)
- Grewer Th., Klais, O.: Exothermic Decomposition: Investigation of the Characteristic. Properties, VDI Verlag Düsseldorf, 1988.
- TRAS 410: „Erkennen und Beherrschen exothermer chemischer Reaktionen“