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A Case Study: Autocatalytic Behavior and its Consideration for a Chemical Process with General application to Handling, Shipping, and Reactive Relief Design

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Abstract

Autocatalysis is a generally well understood phenomenon. However, since autocatalytic molecules do not have a fixed energy release rate for a given temperature, like nth order reactions, additional considerations are required to ensure safe shipping, handling and relief device sizing. Also, unlike nth order reactions, autocatalytic reactions have an induction time and it is associated with reaching a critical concentration of a catalytic species. Once the induction time is exhausted the reaction accelerates even under isothermal conditions (i.e. $dT/dt = f(T,C_{cat})$. Often a thermo-kinetic model is required for adequate hazard evaluation. During model development a first order reaction scheme is often used as a starting point. Such an approach typically leads to an unrealistically high apparent activation energy to get a reasonable fit to the data. Since time impacts the reaction rate, induction times need to be determined to build an accurate kinetic model. Once induction times are determined as a function of temperature, adequate layers of protection and operating discipline can be determined for safe handling. This paper describes: 1) Identification and confirmation of autocatalytic behavior, 2) Induction time model development, and 3) Application to storage, shipping, and reactive relief design. For reactive relief vent sizing, consideration is given not only to credible failure scenarios that may result in relief device activation, but also recovery from contained unplanned events.