Incorporation of Reaction Chemicals Testing Data in Reactivity Hazard Evaluation

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Reactivity Hazard Screening Evaluation

Evaluation of reactivity hazards involves temperature, pressure, and heat rate calculations based on literature or experimental data. Endothermic reactions represent a potential hazard if gaseous or highly volatile products are generated. Exothermic reactions have the potential for a runaway reaction leading to a dramatic increase in temperature, pressure and reaction rate.
Reactivity Hazard Screening Evaluation

Reactions to consider for Hazard Evaluation include (but are not limited to):

- Loss of control of the primary or intended reaction
- Unintended reactions resulting from inadvertent mixing of incompatible materials
- Decomposition of raw materials, intermediates, and products
Key Steps in Reactivity Hazard Analysis

- Initial Hazard Screening from Heat of Reaction per mass and Maximum Reaction Pressure
- Simple Kinetic Modeling of experimental Reactive Chemicals data
- Screening of Reactivity Hazards using Rate Information
- Evaluation of Common Process Upsets
- Reactivity Incident Outcome
## Initial Reactivity Hazard Screening Evaluation

### Categorization of reactivity hazard from Heat of Reaction per Mass

<table>
<thead>
<tr>
<th>Reactivity Hazard</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low to Medium Energy Release Potential</td>
<td>Less exothermic than – 100 Joule/gram corresponding to an adiabatic temperature rise less than 50 C</td>
</tr>
<tr>
<td>High Energy Release Potential</td>
<td>Between -100 and -1000 Joule/gram. In this region, reaction vapor pressure and rate may result in catastrophic failure of process equipment and vessels.</td>
</tr>
<tr>
<td>Potential Explosive</td>
<td>More exothermic than -1000 Joule/gram. Reactions capable of deflagration and detonation.</td>
</tr>
</tbody>
</table>
Initial Reactivity Hazard Screening Evaluation

Estimation of the maximum reaction temperature and pressure provides a useful initial reactivity hazard screen:

- Could the maximum pressure exceed the equipment design such that catastrophic failure or rupture might occur?
- Could the maximum pressure exceed the relief device set pressure resulting in a hazardous chemical release?
The Maximum Reaction Temperature, $T_{\text{Max}}$, may be estimated from the exothermic heat of reaction and heat capacity of the reaction mixture by:

$$T_{\text{Max}} = T_0 + \Delta H_r / C_S$$

where:
- $\Delta H_r$ = reaction heat per mass
- $C_S$ = average heat capacity of reaction mixture
- $T_0$ = initial reaction temperature

The initial temperature, $T_0$, is typically selected as the higher of operating temperature, ambient temperature, heating media temperature, or temperature, which could be attained during upset conditions.
For reactions with products of similar or greater volatility relative to the initial reaction mixture, the **Maximum Reaction Pressure** occurs at the maximum reaction temperature. Pressure for a liquid phase reaction may be simply correlated by:

\[ P = P_{Pad} \left( \frac{T}{T_{P0}} \right) + P_{sat} + \kappa \frac{V_L R T}{V_V} \]

where:
- \( P \) = reaction pressure
- \( P_{Pad} \) = initial gas pad pressure
- \( R \) = Gas Law Constant
- \( T \) = reaction temperature (°K)
- \( T_{P0} \) = initial gas pad temperature
- \( V_V \) = volume vapor in equipment
- \( V_L \) = volume liquid in equipment
- \( \kappa \) = moles of gas produced per volume liquid
- \( P_{sat} \) = vapor pressure of reaction mixture
Once a reaction is considered hazardous due to excessive total pressure or total heat per mass, additional screening may require calculations of reaction rate under normal and process upset conditions.

Four simple models of interest are:

- Simple “n” Order
- Autocatalytic
- Multiple Independent Reactions
- Multiple Consecutive Reactions
Simple Kinetic Modeling of Experimental RC data

Simple "n" Order:  $A \rightarrow C$

Rate, $-\frac{d[A]}{dt} = k \ [A]^n$

Conversion, $\chi = 1 - \frac{[A]}{[A]_0}$

Simple Autocatalytic:  $A + C \rightarrow C + C$

Rate, $-\frac{d[A]}{dt} = k \ [A]^n \ ([C] + [C]_0)$

Conversion, $\chi = 1 - \frac{[A]}{[A]_0}$

where:

- $k$ = rate constant
- $t$ = time
- $[A]$ = concentration of $A$
- $[A]_0$ = initial concentration of $A$
- $n$ = apparent reaction order with respect to reactant $A$
- $[C]_0$ represents the initial concentration of $C$, the Autocatalytic Constant
Simple Kinetic Modeling of Experimental RC data

Independent First Order: \( A \rightarrow C \) and \( B \rightarrow D \)

Rate,

\[
\begin{align*}
-\frac{d[A]}{dt} &= k_A [A] \quad \text{and} \quad -\frac{d[B]}{dt} = k_B [B] \\
\end{align*}
\]

Conversion \( \chi_A = 1 - \frac{[A]}{[A]_0} \)

Conversion \( \chi_B = 1 - \frac{[B]}{[B]_0} = 1 - e^{\left(\frac{k_B}{k_A}\right)\ln\left(\frac{[A]}{[A]_0}\right)} \)

Consecutive First Order: \( A \rightarrow B \rightarrow C \)

Rate,

\[
\begin{align*}
-\frac{d[A]}{dt} &= k_A [A] \quad \text{and} \quad \frac{d[C]}{dt} = k_B [B] \\
\end{align*}
\]

Conversion \( \chi_A = 1 - \frac{[A]}{[A]_0} \)

Conversion \( \chi_B = 1 - \frac{[A]}{[A]_0} - \frac{[B]}{[A]_0} \)

For \( [B]_0 = 0 \),

\[
\frac{[B]}{[A]_0} = \frac{-[A]}{[A]_0} \ln \left(\frac{[A]}{[A]_0}\right) \quad \text{for } k_B/k_A = 1
\]

\[
\frac{[B]}{[A]_0} = \left(\frac{[A]}{[A]_0} - \left(\frac{[A]}{[A]_0}\right)^{\frac{k_B}{k_A}}\right) / \left(k_B/k_A - 1\right) \quad \text{for } k_B/k_A = 1
\]

Assuming \( k_B/k_A \) is constant in the region of interest
Simple Kinetic Modeling of Experimental RC data

Conversion may be correlated to temperature rise from reactive chemicals testing. For an exothermic reaction without external heat input at constant heat capacity,

\[ \chi = \frac{(T - T_{\text{Det}})}{(T_F - T_{\text{Det}})} \]

Conversion may also be related to pressure rise associated with gas generation. For an ideal gas, moles gas generated per liquid volume is related to reaction system pressure by:

\[ \kappa = \frac{(P - P_{\text{sat}} - P_{\text{Pad}} (T/T_0)) (V_V / V_L)}{R T} \]

\[ \chi = \frac{\kappa}{\kappa_T} \] where \( \kappa_T \) represents the total observed gas formation.
The rate constant, $k$, may be expressed as an exponential function of the reciprocal of absolute temperature per the Arrhenius equation:

$$k = r_0 e^{-\left(\frac{\Delta E}{R} \left(\frac{1}{T_{\text{Det}}} - \frac{1}{T}\right)\right)}$$

where:
- $r_0$ = initial rate at concentration $[A]_0$ and temperature $T_{\text{Det}}$
- $T$ = reaction temperature ($^0K$)
- $T_{\text{Det}}$ = detected onset temperature ($^0K$)
- $\Delta E$ = Activation Energy
- $R$ = gas law constant
The initial rate, $r_0$, and Activation Energy, $\Delta E$, may be determined as a function of conversion for a simple “n” order model at any assumed reaction order by linear regression of:

$$\ln \left( \frac{\text{observed rate}}{(1-\chi)^n} \right) = \ln (r_0) + (\Delta E/R) \left( \frac{1}{T_{\text{Det}}} - \frac{1}{T} \right)$$

Various reaction orders may be assumed to determine which provides a “best” fit. Similar regression analysis may be used for other simple kinetic models.
Simple Kinetic Modeling of experimental RC data

Fit of experimental data from conversion correlated by temperature data or pressure data and estimated gas generation

Effect of initial gas pad

Effect of highly volatile or gaseous products
Simple Kinetic Modeling of experimental RC data

Often a simple zero or first order kinetic model provides sufficient accuracy in the region of interest for screening evaluation of reactivity hazards.
A key to managing reactivity hazard for an exothermic reaction is maintaining a normal operating temperature below the temperature at which reaction heat gain exceeds heat loss to the surroundings. Beyond the Temperature of No Return, if no action is taken, the reaction will proceed to a maximum rate.

\[
\text{Heat Gain from Reaction} = a e^{-\Delta E / RT}
\]

\[
\text{Heat Loss to Surroundings} = U A \Delta T
\]

\text{Temperature of No Return, } T_{NR}
Screening of Reactivity Hazards using Rate Information

The **Temperature of No Return** is evaluated from the reaction kinetic model as:

$$T_{NR} = \frac{1}{R \ln \left( \frac{q_0}{q_{NR}} \right) + \frac{1}{\Delta E} + \frac{1}{T_{Det}}}$$

where:

- $\Delta E$ = reaction Activation Energy
- $T_{Det}$ = detected onset temperature ($^\circ$K)
- $R$ = Gas Law Constant
- $q_0$ = initial reaction self heat rate (corresponding to initial reaction rate, $r_0$, at $T_{Det}$)
- $q_{NR}$ = heat loss rate at $T_{NR} = \frac{U A (T_{NR} - T_S)}{M}$

and,

- $U$ = heat loss coefficient
- $A$ = surface area
- $T_S$ = temperature of surroundings
- $M$ = reaction mass
Screening of Reactivity Hazards using Rate Information

The **Time to Maximum Rate**, $t_{MR}$, from any initial temperature may be estimated by integrating the appropriate kinetic rate model. It gives an indication of time frame in which action must be taken to regain control of the reaction system.

For a simple zero order model, the time to maximum rate from any initial temperature is:

$$t_{MR} = \frac{R T_i^2}{q_i \Delta E}$$

where:
- $T_i = \text{initial temperature (}^\circ\text{K)}$
- $q_i = \text{adiabatic self heat rate at the initial temperature (}^\circ\text{K/min)}$
The Maximum Heat Rate or “Power Density” of for an adiabatic runaway reaction may also be useful screening parameter for reactivity. For a zero-order reaction:

\[
\ln \left( \frac{q_{\text{max}}}{q_0} \right) = \frac{(T_F - T_0) \Delta E}{R \ T_0 \ T_F} = \frac{\Delta H_r \ \Delta E}{R \ C_S \ T_0 \ T_F}
\]

where:

- \( \Delta E \) = reaction Activation Energy
- \( \Delta H_r \) = heat of reaction per mass
- \( C_S \) = average heat capacity
- \( R \) = Gas Law Constant
- \( T_0, T_F \) = initial and final temperature (°K)
- \( q_{\text{max}}, q_0 \) = heat rate per mass at maximum and initial conditions
For reaction systems exhibiting **Autocatalytic Behavior:**

- Chemicals may appear to be thermally stable due to an “induction time”.
- The self-heat rate is near zero as time or conversion approaches zero and accelerates to a maximum under isothermal conditions.
- Often results in an unusually high Activation Energy for simple 1st order fit to temperature rate data.
Autocatalytic Behavior may also result from consecutive reactions. In the example below, gas generation was detected at a temperature less than the exothermic detected onset temperature.

Dramatic increase in self heat rate at low conversion is an indicator of Autocatalytic Behavior.
Evaluation of Common Process Upsets on Reactivity Hazard

In some cases, screening evaluation for the impact of a process upset to a reaction may be obtained by adjustment of appropriate kinetic parameters.

Common process upsets of interest are:

- External heat plus reaction
- Change in heat of reaction per mass
- Introduction of a catalytic impurity
- “Pooling” of reactants
Evaluation of Common Process Upsets on Reactivity Hazard

External heat may result from a heat transfer surface, mechanical energy such as an agitator or circulating pump, or fire. The primary impact of **External Heat Input** is an increase in temperature without consuming reactants.

Data Fit at $n=2$:
- $R_0 = 0.0305 \, \text{C/min}$
- $T_{det} = 85 \, \text{C}$
- $\Delta E = 22.1 \, \text{Kcal/mol}$
A change in **Heat of Reaction per Mass** may be the result of scale-up since Thermal Inertia (loss of reaction heat to equipment or sample container) impact is less for larger equipment or the result of miss loading of reactants or solvents.

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**Observed** temperature rise higher with increased reactant concentration

**RC Data Reaction Modeling**

**Effect of Concentration**

<table>
<thead>
<tr>
<th>Reaction Rate</th>
<th>Temperature Rate (C/min)</th>
<th>20% AIBN, Fit at $\Phi=2.19$</th>
<th>15% AIBN, Fit at $\Phi=2.46$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_0$</td>
<td>$T_{Det}$</td>
<td>$\Delta E$</td>
<td>$\Delta \theta_{obs}$</td>
</tr>
<tr>
<td>0.0065</td>
<td>47</td>
<td>29.3</td>
<td>66</td>
</tr>
<tr>
<td>0.015</td>
<td>33.9</td>
<td>38</td>
<td></td>
</tr>
</tbody>
</table>

Maximum temperature and heat rate higher at increased concentration
Evaluation of Common Process Upsets on Reactivity Hazard

Introduction of a Catalytic Impurity may significantly increase the rate constant and overall self heat rate for exothermic reactions.

Observed self heat rate at the same temperature is higher with catalyst or catalytic impurity.
The undesired outcome associated with reactivity hazards includes equipment or vessel failure (physical explosion), release of stored chemical energy (chemical explosion) or relief device activation.

- The sudden release of chemical or pressure-volume energy may produce a shock wave and accelerate equipment fragments.
- Relief device activation may result in the release of toxic or flammable materials.
Summary and Conclusions

- The **Heat of Reaction per Mass** is a key initial screening parameter that may help identify hazard potential. Estimation of the **Maximum Reaction Pressure** provides means to determine if process equipment is designed for containment of a runaway reaction.

- **Simple reaction models** may be used for correlation and extrapolation of experimental reactive chemical data. Often a simple zero or first order model provides sufficient accuracy in the region of interest for screening of reactivity hazards including identifying autocatalytic behavior.
Summary and Conclusions

- Various screening parameters such as Time to Maximum Rate and Temperature of No Return may be used to help identify safe operating limits.

- The impact of common Process Upsets such as external heat input, change in reactant concentration, catalytic impurities, and “pooling” of reactants on reactivity hazards may also be evaluated through a combination of reactive chemicals testing and simple modeling.
Reactivity Hazard Evaluation

Key References