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«Adiabatic» Temperature Rise in Systems with Gas Release

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This paper shows that under certain conditions, adiabatic tests which are carried out in closed test containments do not reveal the “worst case” in terms of adiabatic temperature rise.
If some of the products of the reaction driving the run-away are gases, the temperature of the reaction mass will increase more in open systems, where these gases can escape. This is because the residual mass which has to be heated by the reaction energy decreases.
The effect depends on the kinetics, the heat capacity of the solids and the gases and on the mass fraction of non-condensable gases. The effect is particularly high for self-reactive substances and explosives.
The paper presents the thermodynamic relations, which allow the identification of cases where open systems would be more conservative together with illustrative simulations.

1. Introduction

Adiabatic tests are widely used in the risk assessment of chemical and physical processes. The concept of a hypothetical adiabatic temperature increase ΔT_{adia} as a result of the transformation of chemical reaction energy into heat during a run-away reaction has been applied successfully (TRAS 410, Stoessel):

$$\Delta T_{adia} = \frac{\Delta H}{C} \tag{1}$$

Equation (1) is based on the assumption that the reaction mass and the heat capacity of the reaction mixture are constant during the run-away process. The first condition is true for closed, non-vented systems, and is clearly not true in open systems, if solid or liquid starting materials are converted into escaping gases. The second condition is potentially not fulfilled in both systems
In this approach adiabatic conditions are considered to be a “worst case”, and therefore adiabatic test methods are widely used to determine relevant thermochemical parameters like TMR_{ad} (Time to Maximum Rate) and ΔT_{adia} (Temperature Rise).
Adiabatic conditions by definition do not allow the exchange of energy between a reaction system and the environment. The exchange of matter would have an even greater effect and therefore closed systems are used to characterize thermal run-away reactions. Here the ratio between the heat capacity of the reaction mass and that of the container must be as high as possible (Phi-factor close to 1) to eliminate a heat sink in the container.
In this paper expressions like “adiabatic” or “ΔT_{adia}“ are to be understood to mean “with negligible heat exchange between the reaction mixture and environment”.
If the decomposition reaction driving the thermal run-away produces non-condensable gases, the closed systems might not reflect “worst case conditions”. ΔT_{adia} may be larger in open systems, where the gases can escape for two reasons:

a) Energy produced by the reaction is distributed only on the residual – and smaller – reaction mass. In processes with large gas production this loss of mass dominates changes of specific heat. In contrast to differences in specific heat of educts and products, which remain within a limited range, the effect of escaping mass may cause a considerably larger increase of ΔT_{adia}.
b) Reaction is not “blocked” due the pressure build-up in the vessel.

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2. Energy Balance

Assume a decomposition reaction of a solid A into a solid B and a gas G:

$$A \rightarrow B + G \tag{2}$$

The mass fraction p converted into a gas is

$$p = m_{GF}/m_{A0} = M_G/M_A \ (equimolar\ case) \tag{3}$$

2.1 Closed System

Initially the reaction mass m_{A0} is at the starting temperature T_0. In the closed system, this will be converted into solid $m_{BF} = (1-p) \times m_{A0}$ and gas $m_{GF} = p \times m_{A0}$ at $T_0 + \Delta T_{adia}(closed)$.

$$\Delta H\ m_{A0} = [m_{BF} C_{VB} + m_{GF} C_{VG}]\ \Delta T_{adia}(closed) \tag{3}$$

$$\Delta T_{adia}(closed) = \frac{\Delta H}{[(1-p)\ C_{VB} + p\ C_{VG}]} \tag{4}$$

2.2 Open System

In the open system, the final state is different: There will be the solid $m_{BF} = (1-p) \times m_{A0}$ at $T_0 + \Delta T_{adia}(open)$ *and the gas* $m_{GF} = p \times m_{A0}$ at $T_0 + \gamma \times \Delta T_{adia}(open)$, where $\gamma < 1$ because the gas will escape during the run away and therefore have an average temperature below the final temperature of the remaining solid.

$$\Delta H\ m_{A0} = [m_{BF}\ C_{PB} + \gamma\ m_{GF}\ C_{PG}]\ \ \Delta T_{adia}(open) \tag{5}$$

$$\Delta T_{adia}(open) = \frac{\Delta H}{[(1-p)\ C_{PB} + \gamma\ p\ C_{PG}]} \tag{6}$$

The relation between the heat capacities is

for the solid: $C_{PB} \approx C_{VB}$ (7)

for a bimolecular gas: $C_{PG} \approx 1.4\ C_{VG}$ (8)

Which results in

$$\frac{\Delta T_{adia}(open)}{\Delta T_{adia}(closed)} = \frac{[(1-p)\ C_{VB} + p\ C_{VG}]}{[(1-p)\ C_{VB} + 1.4\,\gamma\ p\ C_{VG}]} \tag{9}$$

$$if\ p > 0\ and\ \ 1.4\,\gamma < 1\ \ \rightarrow\ \frac{\Delta T_{adia}(open)}{\Delta T_{adia}(closed)} > 1 \tag{10}$$

Because in the initial phase of the run-away reaction the heat capacity of the reaction mass is larger than toward the end, the average temperature increase of the gas will be smaller than ½ x $\Delta T_{adia}(open)$, in other words:

$$\gamma < {}^{1}\!/_{2}\ \rightarrow\ 1.4\,\gamma < 0.7 \rightarrow \frac{\Delta T_{adia}(open)}{\Delta T_{adia}(closed)} > 1 \tag{11}$$

3. Dynamic Simulation

3.1 General

Dynamic models of the system with gas release are rather simple and can be calculated with any simulation software. Care has to be taken, however, of the integration routines. The combination of Arrhenius acceleration and additional temperature increase due to gas release, can cause extremely large temperature increase rates. Simulations presented here were carried out using Berkeley Madonna Software (www.berkeleymadonna.com) with variable integration increment, such that maximal temperature change in any computational step was smaller than 0,01 K. This leads in the case described in Section 2 to integration time increments as small as 4 microseconds.

3.2 Assumptions:

- The system is homogeneous.
- There is no heat exchange to the walls or environment (ideal adiabatic conditions, worst case).
- Gases are released from the system with the temperature at which they were formed (no heat exchange between gaseous materials or vapours and the content).
- Escaping gases do not carry away solid or liquid material.
- Temperature dependence of specific heats is neglected.

We have also developed models to simulate processes which do not fulfill all these conditions. They are suitable for the study of special cases and need additional physical data. Their description exceeds the scope of this paper.

3.3 **Kinetic Equations** (for the reaction in expression (2))

Initial Conditions:

$$m_A(0) = m_{A0}\,;\; m_B(0) = 0; m_G(0) = 0;\; T(0) = T_0 \tag{12}$$

Heat Production Rate

$$q(T(t)) = m_{A0}\, q'(T_{ref})\, exp\left[-\frac{E_a}{R}\left(\frac{1}{(T(t)+273)} - \frac{1}{(T_{ref}+273)}\right)\right] \frac{m_A(t)}{m_A(t) + m_B(t)} \tag{13}$$

Reaction Heat (Kirchhoff Law)

$$closed\text{: } \Delta H\big(T(t)\big) = \Delta H(T_0) - (T(t) - T_0)\{(1-p)\, C_{VB} + p\, C_{VG} - C_{VA}\}. \tag{14}$$

$$open\text{: } \Delta H\big(T(t)\big) = \Delta H(T_0) - (T(t) - T_0)\{(1-p)\, C_{PB} + pC_{PG} - C_{PA}\} \tag{15}$$

Reaction Rate

$$\frac{dm_A}{dt}(t) = \frac{-q(T(t))}{\Delta H(T(t))}\,;\; \frac{dm_B}{dt}(t) = -(1-p)\,\frac{dm_A}{dt}(t)\,;\; \frac{dm_G}{dt}(t) = -p\,\frac{dm_A}{dt}(t) \tag{16}$$

Temperature Increase

$$closed: \;\frac{dT}{dt}(t) = \frac{q(T(t))}{m_A(t)\, C_{VA} + m_B(t)\, C_{VB} + m_G(t)\, C_{VG}} \tag{17}$$

$$open: \;\frac{dT}{dt}(t) = \frac{q(T(t))}{m_A(t)\, C_{PA} + m_B(t)\, C_{PB}} \tag{18}$$

The relevant differences between closed and open systems are

- The use of C_{PX} in contrast to C_{VX}
- The missing heat capacity of the gas in equation 18, as it is assumed that the gas is removed from the system immediately after release. This is a simplification of the real situation, because in practice the escaping gas will be heated while passing through the remaining solid to the vent opening.

4. Example

To demonstrate the effect, a dynamic simulation with the following parameter was carried out:

p	0.5	Ea	99720 kJ mol^{-1}
C_{PA}=C_{VA}	1.80 kJ kg^{-1} K^{-1}	m_{A0}	1 kg
C_{PB}=C_{PA}	1.80 kJ kg^{-1} K^{-1}	ΔH_0	500 kJ kg^{-1}
C_{PG}	1.00 kJ kg^{-1} K^{-1}	T_0	100 °C
C_{VG}	0.71 kJ kg^{-1} K^{-1}	T_{ref}	100 °C
		q'_{ref}	1 W kg^{-1}

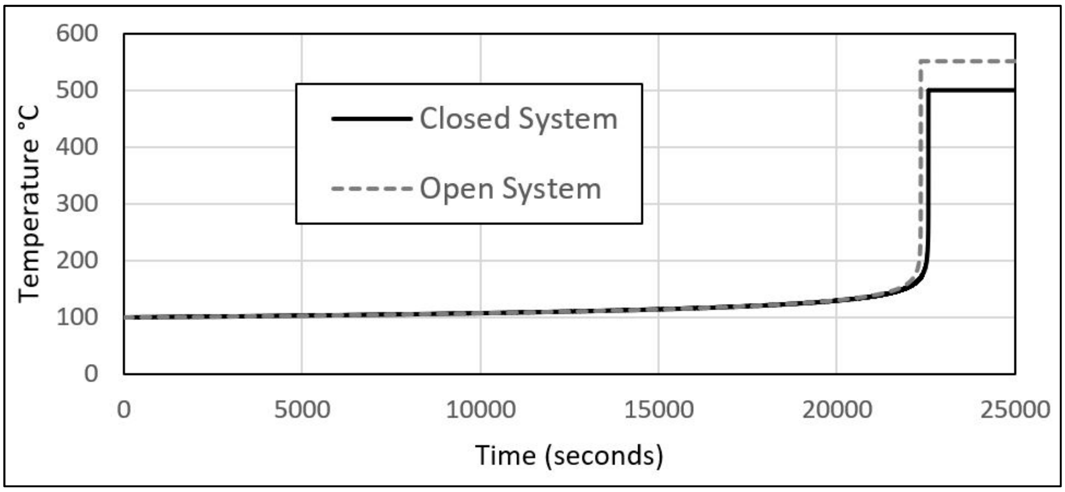

Figure 1: Adiabatic temperature curve for a closed and open system with a gas mass fraction p =0.5

The results show the behaviour expected from the heat balance considerations: The adiabatic temperature increase was higher if non-condensable gas is produced during the reaction and escapes from the system.

5. The Effect of the Gas Mass Fraction p

Using the same thermodynamic parameters as above, the adiabatic temperature increase for closed and open systems were calculated for different gas mass fractions.

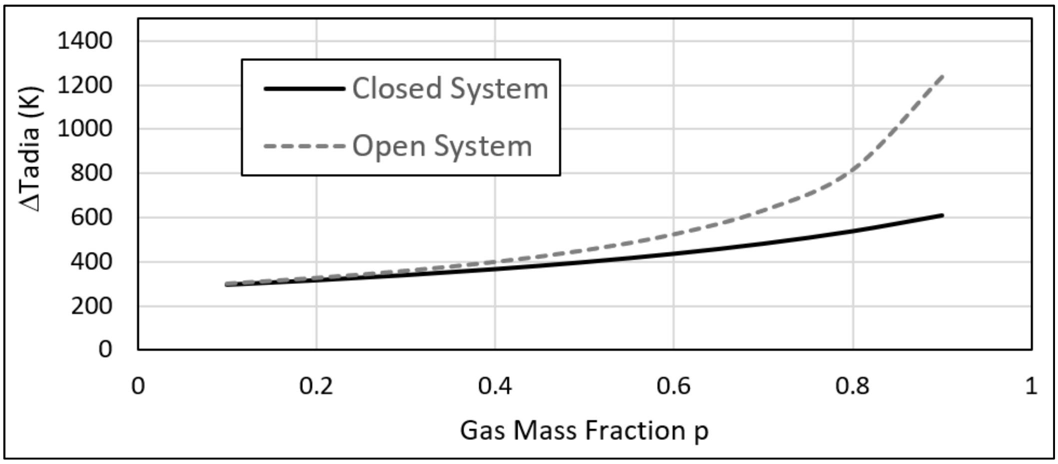

Figure 2: Effect of of the Gas Mass Fraction p on ΔT_{adia} (parameters see section 4)

6. Acceleration

Decomposition of high energetic materials in closed or open vessel show very large difference in the rate of production of gases and vapors. The maximum gas production rate for the reaction as described in Section 4 and with p=0.9 is 3305 kg s^{-1} for open and 64.8 kg s^{-1} for closed systems.

Thus, in open systems the temperature not only increases to higher values, the increase is also accelerated, leading to shorter time to maximum rate (TMR) and higher gas production rates.

The influence on TMR is not safety relevant, since the major part of the conversion takes place within the relative short time toward the end of the process.

There is, however, a significant impact of gas release on the maximum reaction rate itself. If a close system is changed to an open system, e.g. in case of venting, the reaction rate may drastically increase due to the change of heat capacity. This may be an explanation of reports about «violent explosions», often in connection with high gas production (Bretherick).

7. Release of Vapors

Reduction of the reaction mass in the containment can be caused also by release of vapors. It will be often argued that measurements in open test tubes will yield lower adiabatic temperature rise due to evaporation. Release of vapour, however, increases the temperature rise and can partially compensate the heat spent for evaporation. In combination with gas release the resulting temperature increase may be higher in an open system.

Figure 3 shows run away curves in a system with 9% (w/w) solvent (toluene). The evaporation leads, as expected, to a longer TMR (delay), but ultimately the adiabatic temperature increase is higher in the open system than in the closed system.

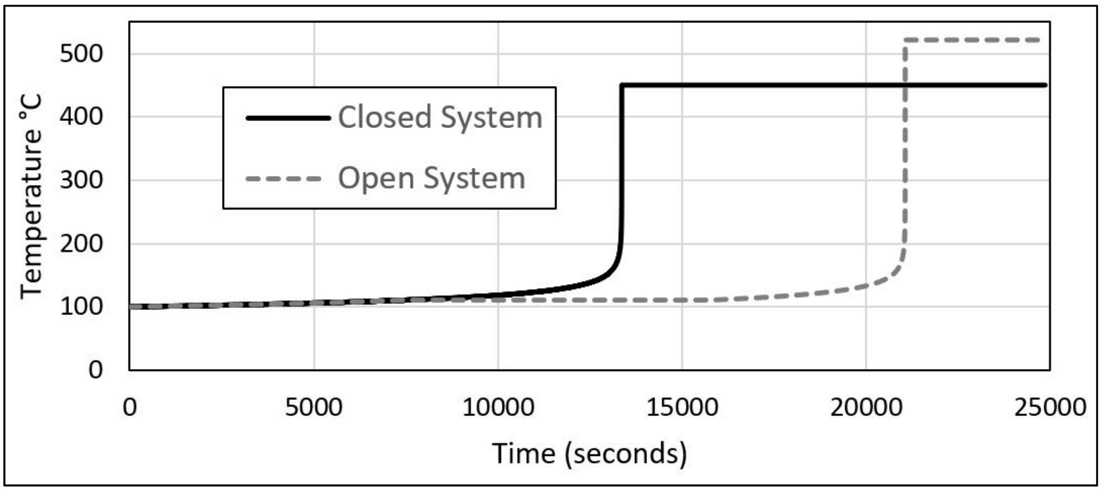

Figure 3: Effect of solvent evaporation on the adiabatic temperature curve in open and closed systems

The simulation parameters are essentially identical to those in sections 4 and 5 for p=0.5. However the model is extended to cover the presence of solvent (toluene) and its evaporation. Parameters of toluene in following table are designated by "TOL", l = liquid, g = gas

Reaction Scheme $A + TOL(l) \rightarrow B + G + TOL(g)$

m_{A0}	1.0 kg	$C_{P,TOL,g}$	1.49 kJ kg^{-1} K^{-1}	ΔH_0	500 kJ kg^{-1}
m_{TOL0}	0.1 kg	$C_{V,TOL,g}$	1.00 kJ kg^{-1} K^{-1}	$\Delta H_{V,TOL}$	360 kJ kg^{-1}
$C_{P,TOL,l}$	1.80 kJ kg^{-1} K^{-1}	Ea	99720 kJ mol^{-1}	$T_{boil,\ TOL}$	111 °C

8. Identification and Evaluation of Gas Release

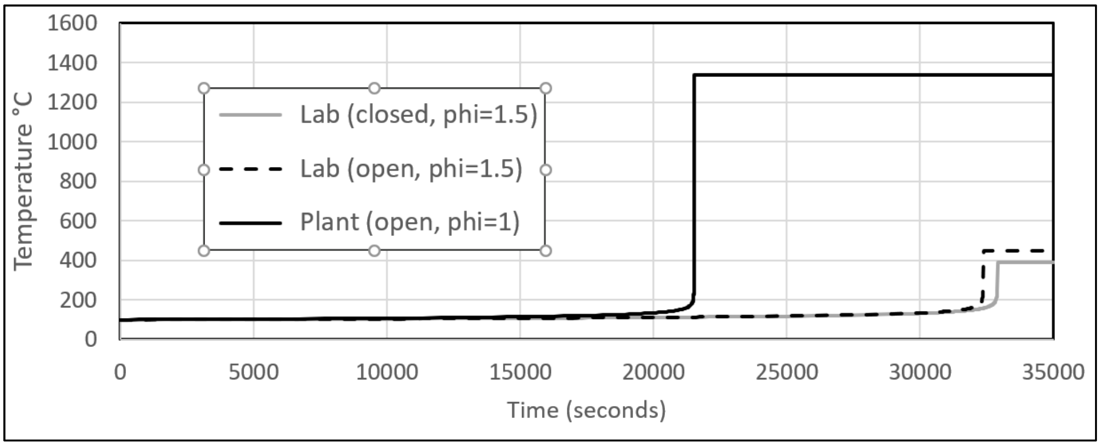

Figure 4: Comparison of temperature increase in laboratory instruments with Phi factor 1.5 and large real equipment with Phi factor 1. In this simulation p = 0.9; other parameters are the same as in Section 4.

Production of gas during the reaction can be easily detected by weighing the test tube before and after the measurement. Identification of higher temperature increase and especially of further dangerous effects is difficult. Unfortunately, even experiments in an open containment does not always reveal the potential hazard. This is partly due to thermal inertia (Phi factor) of laboratory instruments. (Figure 4).

9. Conclusions

Changes in the heat capacity during a reaction have a significant influence on the adiabatic behaviour of reactive systems. Loss of mass due to escaping gas and/or vapour reduces the heat capacity of the content of the vessel and thus leads to higher adiabatic temperature increase and acceleration of the adiabatic reaction. The higher adiabatic temperature increase due to escaped gas can also trigger the consecutive exothermic reaction. Depending on thermokinetic parameters such danger can be overseen with measurement in closed system. A more violent behaviour may result.

The effect is most pronounced in systems producing high quantities of non-condensable gases, i.e. self-reactive substances or explosives.

While gas production is quite common for decomposition reactions, the effect is rarely observed in experimental practice, because it cannot be directly seen by measurements in closed containments. Some of the effects can be overseen even by measurements in open systems due to generally higher value of Phi factor on laboratory scale. In addition, many decompositions are highly energetic and adiabatic tests usually cannot trace the adiabatic increase to the very end. The gas production can be, however, detected either by pressure measurement or by mass balance after opening the system.

Symbols

C	*Specific Heat Capacity [J kg^{-1} K^{-1}]*
C_{PX}	*Specific heat Capacity of Component X at constant pressure [J kg^{-1} K^{-1}]*
C_{VX}	*Specific heat Capacity of Component X at constant volume [J kg^{-1} K^{-1}]*
E_a	*Activation Energy [J mol^{-1}]*
m_{A0}	*Initial Mass of Component 0 [kg]*
Mx	*Molecular Weight of X, X = A, B, G, Z [kg/kmole]*
m_X	*Mass of Component X; X =A,B,G,Z; G = gas [kg], suffix F = final*
p	*Mass Fraction of Gas formed (dimensionless)*
$q(T)$	*Heat Production Rate at Temperature T [W]*
$q'(T_{ref})$	*Specific Heat Production Rate at Reference Temperature [W/kg]*
R	*Gas Constant (8.313 J mol^{-1} K^{-1})*
T	*Temperature of the reaction mixture [°C]*
T_0	*Initial Temperature of the adiabatic test [°C]*
T_{ref}	*Reference Temperature for heat production rate (typically onset in DSC) [°C]*
ΔH	*Specific Heat of Reaction [J kg^{-1}], exotherm = positive values*
ΔT_{adia}	*Adiabatic Temperature Rise [K]*
ΔH_{Evap}	*Specific Heat of Evaporation [J kg^{-1}]*

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