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Comments on the Letter to the Editor from M. Malow, U. Krause and K.D. Wehrstedt concerning the paper of H. Fierz: Influence of heat transport mechanism on transport classification by SADT-measurement as measured by the Dewar-method

The authors quote several cases where the method in question works, amongst them many solid peroxides. The method should however be applicable not only for peroxides, but for a very broad range of substances to be transported. In most cases their thermochemical properties are not fully known. For the interpretation of the test therefore a set of physical and chemical parameters should be chosen which covers also values at the end of the range and a possible worst case.

For a fixed volume as in a Dewar vessel, density will influence mass and therefore the cooling curve of the Dewar vessel. From this it can be shown (see Appendix A) that the square of r_{crit} is proportional to the heat conductivity only of the bulk substance. The heat conductivity of the bulk substance itself depends on its void volume.

The authors quote the book of Grewer for calculating the extrapolated bulk powder size [1, p. 44]. The basis of this calculation is an assumed heat loss of the Dewar vessel of 0.04 W/kg K ([1, p. 103, Table 3.2]. However, the method given in the UN recommendations [2] assumes a heat loss of 0.08 to 0.1 W/kg K for the Dewar vessel. Using this value, an extrapolated volume of 20 l (and not of 80 l) is obtained.

I therefore agree fully with the conclusion of the authors that a more detailed investigation of the influence of the physical and chemical parameters is needed. It is hoped that such studies eventually will lead to a procedure that satisfies both the practical needs and the theoretical concepts.

Appendix A. Does bulk density influence the predicted volume size in the UN-Test H4?

The cooling time constant τ_C of a Dewar vessel is determined by an experiment using a calibration substance like water or dimethylphtalate with subscript C:

$$\tau_C = \frac{V_D \rho_C c_{p_C} + m_D c_{p_D}}{h_D A_D} = \frac{V_D \rho_C c_{p_C}}{h_D A_D}\left(1 + \frac{m_D c_{p_D}}{V_D \rho_C c_{p_C}}\right) \tag{A.1}$$

$$h_D A_D = \frac{V_D \rho_C c_{p_C}}{\tau_C}\left(1 + \frac{m_D c_{p_D}}{V_D \rho_C c_{p_C}}\right) \tag{A.1a}$$

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where ρ_C and $c_{p\mathrm{C}}$ are the specific density and specific heat capacity of the calibration substance, h_D, A_D and V_D are the heat transfer coefficients of the Dewar, its heat exchange area and its volume, m_D the mass of the Dewar in contact with the substance and $c_{p\mathrm{D}}$ its specific heat capacity.

For an actual substance in bulk with density ρ_B and specific heat capacity $c_{p\mathrm{B}}$ a different τ must be determined, which we call τ_B. This can be done by calculation from τ_C via Eq. (A.1a) and a correction for the heat capacity of the Dewar vessel:

$$\tau_\mathrm{B} = \frac{V_\mathrm{D}\rho_\mathrm{B}c_{p\mathrm{B}}}{h_\mathrm{D}A_\mathrm{D}}\left(1 + \frac{m_\mathrm{D}c_{p\mathrm{D}}}{V_\mathrm{D}\rho_\mathrm{B}c_{p\mathrm{B}}}\right)^{-1} \tag{A.2}$$

where we assume that the heat transfer coefficient h_D does not change when going from the calibration substance to the bulk.

For each chemically reacting bulk system, there exists a time to maximum rate under adiabatic conditions

$$\mathrm{TMR}_\mathrm{ad} = \frac{RT^2c_p}{E_\mathrm{a}\dot{q}} \tag{A.2a}$$

where R is the universal gas constant and E_a and $\dot{q}$ are the activation energy and the heat release rate of the chemical process at the temperature T.

The critical value for the TMR_ad for this bulk substance can be calculated as

$$\mathrm{TMR}_{\mathrm{crit\,B}} = \mathrm{e}\tau_\mathrm{B} \tag{A.3}$$

In this case, the heat released by the chemical reaction $\dot{q}_\mathrm{crit}$ can just be dissipated by the system. We assume that this bulk shows Newtonian cooling in the Dewar. It is however not clear whether this assumption is always valid.

Combining Eqs. (A.2) and (A.3) we obtain

$$\mathrm{TMR}_{\mathrm{crit\,B}} = \mathrm{e}\,\frac{V_\mathrm{D}\rho_\mathrm{B}c_{p\mathrm{B}}}{h_\mathrm{D}A_\mathrm{D}}\left(1 + \frac{m_\mathrm{D}c_{p\mathrm{D}}}{V_\mathrm{D}\rho_\mathrm{B}c_{p\mathrm{B}}}\right)^{-1} \tag{A.4}$$

Now we switch to the bulk container and calculate the critical radius of a sphere after Frank–Kamenetskii [1, p. 44]:

$$r_{\mathrm{crit\,B}} = \sqrt{3.32\,\mathrm{TMR}_{\mathrm{crit\,B}}\frac{k_\mathrm{B}}{\rho_\mathrm{B}c_{p\mathrm{B}}}} \tag{A.5}$$

Inserting Eq. (A.4) into Eq. (A.5) we obtain

$$r_\mathrm{crit} = \sqrt{3.32\,\mathrm{e}\,\frac{V_\mathrm{D}\rho_\mathrm{B}c_{p\mathrm{B}}}{h_\mathrm{D}A_\mathrm{D}}\left(1 + \frac{m_\mathrm{D}c_{p\mathrm{D}}}{V_\mathrm{D}\rho_\mathrm{B}c_{p\mathrm{B}}}\right)^{-1}\frac{k_\mathrm{B}}{\rho_\mathrm{B}c_{p\mathrm{B}}}} \tag{A.6}$$

and this gives finally

$$r_\mathrm{crit} = \sqrt{3.32\,\mathrm{e}\,\frac{V_\mathrm{D}k_\mathrm{B}}{h_\mathrm{D}A_\mathrm{D}}\left(1 + \frac{m_\mathrm{D}c_{p\mathrm{D}}}{V_\mathrm{D}\rho_\mathrm{B}c_{p\mathrm{B}}}\right)^{-1}} \tag{A.7}$$

For the term

$$\frac{m_\mathrm{D} c_{p_\mathrm{D}}}{V_\mathrm{D} \rho_\mathrm{B} c_{p_\mathrm{B}}}$$

approaching zero, which means that the heat capacity of the Dewar vessel can be neglected. Eq. (A.7) reduces to

$$r_\mathrm{crit} = \sqrt{3.32\,\mathrm{e}\,\frac{V_\mathrm{D} k_\mathrm{B}}{h_\mathrm{D} A_\mathrm{D}}} \tag{A.8}$$

References

[1] Th. Grewer, Thermal Hazards of Chemical Reactions, Industrial Safety Series, vol. 4, Elsevier, Amsterdam, 1994.

[2] Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Section 28.4.4, Test H.4, United Nations, New York, 1999.

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