Influence of heat transport mechanisms on transport classification by SADT-measurement as measured by the Dewar-method

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Abstract

The self-accelerating decomposition temperature (SADT) is according to the United Nations Recommendations on the Transport of Dangerous Goods needed for transport classification of goods as class 4.1 (self-reactive). One of the methods recommended to determine the SADT is the Dewar-method.

The method is well suited to assess the transport stability of liquids, whereas for solids the assessment errs on the unsafe side. The differences in heat transfer between solids and liquids are explained using cooling curves and classifying them by their Biot and Fourier-numbers and by applying the theories of Semenov and Frank-Kamenetskii for the critical heat release rates.
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1. Introduction

If a chemical substance is to be transported, it needs a transport classification. The classification system and the corresponding tests are described in the United Nation Recommendations on the Transport of Dangerous Goods [1]. If preliminary tests of a substance show that it should be classed as 4.1 (self-reactive), it is necessary to determine the self-accelerating decomposition temperature (SADT).

One of the methods recommended to determine the SADT is the Dewar-method. The substance to be measured is placed in a 500 ml Dewar vessel and the ambient temperature $T_{ambient}$ chosen so that the temperature difference $\Delta T = T_{Dewar} - T_{ambient} = 6$ K. The method is described in detail in [1].

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This method contains several inconsistencies and also conceptual errors, which make it difficult to apply. Some of them were already treated in [2]. We would like to discuss these difficulties in this paper.

2. Characterisation of a system by cooling

The basic idea behind the use of a Dewar vessel is that this vessel should have a heat loss equivalent to a bigger package used for transporting the substance; in other words, the results can be scaled up.

The cooling of a Dewar vessel including its content is assumed to be Newtonian, that is defined by a time constant τ

$$\Delta T = \Delta T_0 \, e^{-t/\tau} \tag{1}$$

$$\tau = \frac{m \, c_p}{h \, A} \tag{2}$$

where m is the mass, c_p the specific heat capacity, h the heat transfer coefficient in $W/(m^2 \, K)$ and A the heat exchange area in m^2. Alternatively, a transport package showing Newtonian cooling can be characterised by its specific heat loss $\dot{q}_{Loss}$ in $W/(kg \, K)$ as given in Table 1 for dimethylphtalate (DMP):

$$\dot{q}_{Loss} = \frac{c_p}{\tau} = \frac{h \, A}{m} \tag{3}$$

Obviously both the time constant τ and the specific heat loss $\dot{q}_{Loss}$ are properties both of the bulk material and of the vessel or packaging containing it. To understand the cooling characteristics of a packaging containing bulk material, a separation between this bulk material and the packaging must be done. For Newtonian cooling this is possible, because it is assumed that the main resistance to heat transfer lies in the wall. The heat loss of a package can therefore be characterised by its overall heat loss $\dot{Q}_{Loss}$ in W/K. For a known A, an average value for the heat transfer coefficient h can be defined. This can also be done for a Dewar vessel (Fig. 1). For 500 ml Dewars, we determine routinely in our laboratory cooling curves with water and consistently obtain $\dot{q}_{Loss}$ of about 0.04 $W/(kg \, K)$. If we refer this to the inner surface of the vessel, a h of ca. 0.6 $W/(m^2 \, K)$ is obtained, and this value is found consistently also for household insulation flasks.

Table 1
Heat loss per unit mass from packages, IBCS and tanks

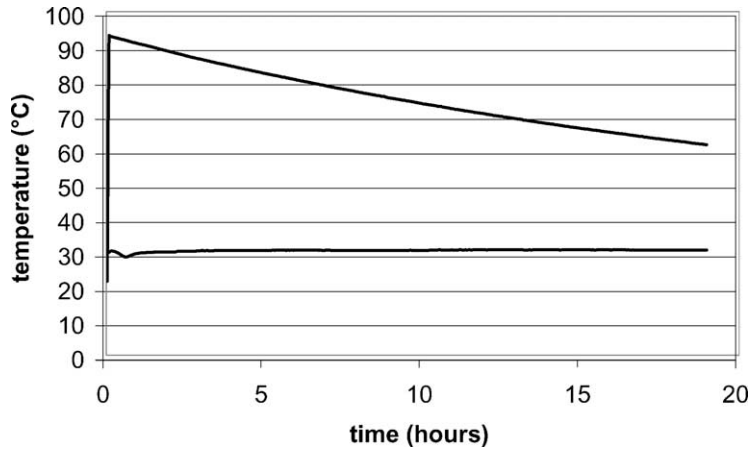| Type of receptacle	Nominal capacity (l)	Filling	Heat loss per unit mass, $\dot{q}_{Loss}$ (mW/(kg K))
For liquids			
1A1	50	47.5 kg DMP	63
For solids			
1G	38	28.0 kg dicyclohexylphtalate (solid)	35

Excerpt from [1].

Fig. 1. Newtonian cooling: cooling curve of a 500 ml Dewar vessel with water. Lower line: ambient temperature; upper line: temperature in Dewar.

The cooling behaviour of packagings or vessels holding liquids can therefore easily both be measured and also scaled up to other dimensions.

When scaling up a package, its τ will increase linearly with the characteristic length of the package l. A doubling of l means therefore an eight-fold increase in volume and a doubling of the time constant.

Assuming a $\dot{q}_{Loss}$ of 0.08 W/(kg K) will make the cooling behaviour of a Dewar vessel equivalent to a 50 l package, whereas 0.04 W/(kg K) makes it equivalent to a 500 l package.

The situation is different for solids (Fig. 2). Heat is transported by conduction only, which leads in general to a temperature gradient within the substance [3]. This means that
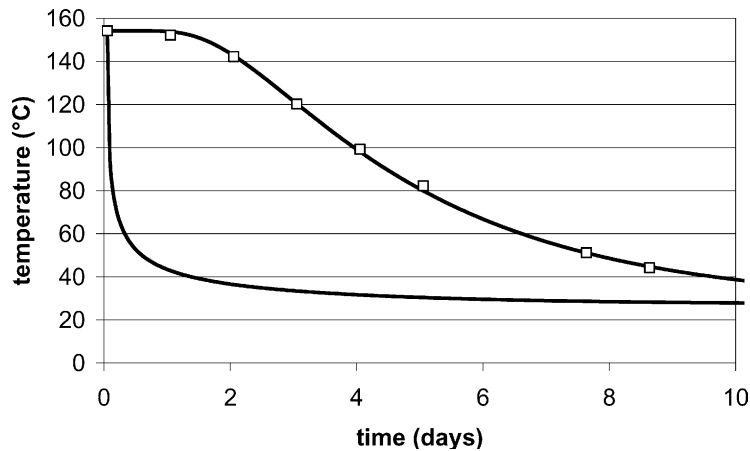

Fig. 2. Cooling of 300 kg of an organic solid. Temperatures were measured in the centre (squares). Temperatures for an equivalent sphere with radius r_0 were calculated for centre (upper curve), and wall (lower curve).

the heat transport is determined by the bulk material and not by the package. Whether the temperature gradient in the bulk is significant or not is defined by the Biot number hl/k. Biot numbers >10 will result in a inhomogeneous temperature distribution and failure of the Newtonian cooling model, whereas with Biot numbers <0.5 Newtonian cooling can be assumed also in solids.

Cooling curves can (for a given geometry) made dimensionless by using instead of time t the so-called Fourier number

$$\mathrm{Fo} = \frac{k}{\rho\, c_\mathrm{p}} \frac{t}{l^2} \tag{4}$$

where ρ is the specific density in kg/l. The same Fo will always produce the same relative temperature change.

These facts have consequences for the scale-up from laboratory scale to big bulk packages:

(a) As the Biot number is proportional to l, heat transport by conduction and therefore, temperature gradients will be more important in big packages than in small ones. For small packages the assumption of a homogeneous temperature distribution and therefore Newtonian cooling is in most cases acceptable, whereas this is definitely not so for big packages. Fig. 1 illustrates the cooling behaviour of a 300 l package with an organic solid.
(b) Cooling time will increase with the square of l.

For higher Fourier numbers for example for Fo >0.2, ΔT will decrease exponentially. Plotting $\ln(\Delta T/\Delta T_0)$ in the centre of a spherical container against Fo, at this region always a slope of -9.8 will result. Formally a τ can be attributed to this slope which would be equivalent to

$$\tau = 0.102 \frac{\rho\, c_\mathrm{p}}{k}\, l^2 \tag{5}$$

and correspondingly an apparent $\dot{q}_\mathrm{Loss}$ can be defined as given in Table 1 for solid dicyclohexylphtalate.

While this apparent $\dot{q}_\mathrm{Loss}$ suggests that the heat transfer mechanism of both a solid and a liquid can be described by the same mechanism, it is important to note that the underlying heat transfer mechanism for liquid dimethylphtalate in Table 1 is different from that for solid dicyclohexylphtalate. Note also that the apparent time constant for dicyclohexylphtalate is position dependent: temperature–time curves off-centre will deliver a different time constant. The description of the cooling process of a solid by a time constant or by the specific heat loss $\dot{q}_\mathrm{Loss}$ of the container is therefore misleading and should be avoided.

3. Critical heat production rate according to Frank-Kamenetskii

For systems which are chemically non-inert but where a reaction with a heat release $\dot{q}$ takes place, a critical heat production $\dot{q}_\mathrm{crit}$ of this reaction can be defined, above which the heat of decomposition can no longer be dissipated, but will accumulate and lead to a thermal

explosion and subsequent destruction of the package [4]:

$$\dot{q}_{\text{crit}} = \delta_{\text{crit}} \frac{k\, R T^2}{\rho\, l^2 E_{\text{a}}} \tag{6}$$

where δ_{crit} is a form factor depending on the geometry of the package.

If the temperature dependence of the decomposition kinetics is known, it will define an upper temperature, above which the package is no longer stable, but will thermally explode. On the other hand, knowing the heat release rate of the decomposition reaction will define an upper limit of the package size. Note that $\dot{q}_{\text{crit}}$ is inversely proportional to the squared characteristic length l of the package.

4. Conclusions

1. The SADT-test using a 500 ml Dewar vessel correctly predicts the thermal behaviour of a 500 l package filled with a liquid, but it will only be representative for an 8 l package filled with a solid.
2. The UN-test H.4 was obviously designed to make a direct scale-up to a predetermined package size possible. This does not work for solids. Extrapolated package sizes for solids are dramatically different from those for liquids.
3. For solids the UN-test H.4 errs grossly on the unsafe side and should therefore not be used.
4. The concept of time constants and specific heat losses for cooling of solids is misleading and should be abandoned. For solids the cooling characteristics of the bulk in its packaging should be determined individually in each case or even better: the theory of Frank-Kamenetskii should be applied.

Appendix A. Model calculation for a spherical system

As mentioned in the introduction to this paper the critical condition for the SADT is a Dewar experiment with $\Delta T = 6\,\text{K}$ at $75\,^\circ\text{C}$. We assume the characteristic dimension, i.e. the radius l of the Dewar vessel to be equal to 0.05 m, its heat transfer coefficient equal to $0.6\,\text{W}/(\text{m}^2\,\text{K})$ and the heat conductivity of the bulk material equal to $0.1\,\text{W}/(\text{m}\,\text{K})$. This gives a Biot number of 0.3. It can therefore be assumed, that after some hours the temperature distribution will be homogeneous within the Dewar vessel. Knowing its specific $\dot{q}_{\text{Loss}}$ the heat production $\dot{q}_{\text{SADT}}$ for $\Delta T = 6\,\text{K}$ can be calculated: $\dot{q}_{\text{SADT}} = 0.04\,\text{W}/(\text{kg}\,\text{K}) \times 6\,\text{K} = 0.24\,\text{W}/\text{l}$.

The radius l of a corresponding non-insulated bulk package containing a solid can be calculated using the concept of the critical heat release rate $\dot{q}_{\text{crit}}$ and setting $\dot{q}_{\text{SADT}} = \dot{q}_{\text{crit}}$. Assuming a value for the activation energy of the reactive system of 90 kJ/mol, a density ρ of $1000\,\text{kg/m}^3$, a heat capacity c_{p} of 2 kJ/(kg K) and a heat conductivity k of $0.1\,\text{W}/(\text{m}\,\text{K})$, l can be calculated as 0.124 m. This corresponds to a volume of a spherical container of 8 l. A heat transfer coefficient at the container wall of $5\,\text{W}/(\text{m}^2\,\text{K})$ is assumed. The Biot number

of the bulk packaging is therefore 4. This shows that heat transport is mainly by conduction and that the assumption of Frank-Kamenetskii is therefore valid.

References

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