Comparative analysis of the methods for SADT determination

A.A. Kossoy *, I.Ya. Sheinman

ChemInform St. Petersburg, CISP Ltd., 14, Dobrolubov Ave., 197198 St. Petersburg, Russia

Available online 28 June 2006

Abstract

The self-accelerating decomposition temperature (SADT) is an important parameter that characterizes thermal safety at transport of self-reactive substances. A great many articles were published focusing on various methodological aspects of SADT determination. Nevertheless there remain several serious problems that require further analysis and solution. Some of them are considered in the paper.

Firstly four methods suggested by the United Nations "Recommendations on the Transport of Dangerous Goods" (TDG) are surveyed in order to reveal their features and limitations.

The inconsistency between two definitions of SADT is discussed afterwards. One definition is the basis for the US SADT test and the heat accumulation storage test (Dewar test), another one is used when the Adiabatic storage test or the Isothermal storage test are applied. It is shown that this inconsistency may result in getting different and, in some cases, unsafe estimates of SADT.

Then the applicability of the Dewar test for determination of SADT for solids is considered. It is shown that this test can be restrictedly applied for solids provided that the appropriate scale-up procedure is available. The advanced method based on the theory of regular cooling mode is proposed, which ensures more reliable results of the Dewar test application.

The last part of the paper demonstrates how the kinetics-based simulation method helps in evaluation of SADT in those complex but practical cases (in particular, stack of packagings) when neither of the methods recommended by TDG can be used.
© 2006 Elsevier B.V. All rights reserved.

Keywords: SADT; Thermal explosion; Reactive chemicals; Mathematical simulation

1. Introduction

The self-accelerating decomposition temperature (the SADT) is an important parameter that characterizes thermal hazard under transport conditions of condensed self-reactive substances. The SADT has been introduced into the international practice by the United Nations "Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria" (TDG) [1]. The Globally Harmonized System (GHS) [2] had inherited the SADT as a classification criterion for self-reactive substances. According to TDG the SADT is defined as "the lowest temperature at which self-accelerating decomposition may occur with a substance in the packaging as used in transport". Important feature of the SADT is that it is not an intrinsic property of a substance but "... a measure of the combined effect of the ambient temperature, decomposition kinetics, packaging size and the heat transfer properties of the substance and its packaging" [1].

If the SADT $\leq 50\,°C$ for organic peroxides and $\leq 55\,°C$ for self-reactive substances, the following control and emergency temperatures are set for a packaging (Table 1).

The Manual recommends four tests for determining the SADT:

1. The United States SADT test (US SADT test) H1.
2. Adiabatic storage test (AST) H2.
3. Isothermal storage test (IST) H3.
4. Heat accumulation storage test (Dewar test) H4.

The H1 test foresees the experimental determination of the SADT for a commercial packaging. The H4 test is also based on experimental determination of the SADT for a small Dewar vessel, which is supposed to be representative for a commercial packaging provided that the special scale-up procedure is used.

The H2 and H3 tests are based on the use of adiabatic and isothermal calorimetric technique respectively with the following estimation of the SADT.

The US SADT test is the only method that gives the direct and, hence, the most reliable answer. Nevertheless it is used rather

* Corresponding author. Tel.: +7 812 303 92 83; fax: +7 812 325 66 17.
E-mail address: kossoy@cisp.spb.ru (A.A. Kossoy).

Nomenclature

a	thermal diffusivity ($a = \lambda/c_p/\rho$, m^2/s)
c_p	specific heat of a product (J/kg/K)
dQ/dt	specific rate of heat generation due to a reaction (W/kg)
E	activation energy (kJ/mol)
h	height of a barrel (m)
$[k_0]$	preexponential factor (s^{-1})
m_p	mass of a product (kg)
Q^∞	heat effect of a reaction (J/kg)
r	radius of a barrel (m)
R	universal gas constant ($R = 8.31$ J/mol/K)
S	surface of heat exchange (m^2)
T	temperature (K)
T_{CR}	critical temperature of thermal explosion (K)
T_e	ambient temperature (K)
$[T_0]$	initial temperature of a product (K)
U	heat transfer coefficient (W/m^2/K)
$(US)/m$	specific heat loss (W/kg/K)
V	volume of a vessel or a package (m^3)
z	autocatalytic constant

Greek letters

α	degree of conversion
$[\Delta T_6]$	the characteristic 6 °C overheat in the middle of a package ($\Delta T_6 = 6$ °C)
λ	thermal conductivity coefficient (W/m/K)
μ_i	roots of the characteristic equation
ρ	product density (kg/m^3)
ω	cooling tempo (s^{-1})

rarely because of its expensiveness. Moreover this test can be applied only for packagings of up to 220 L so that large tanks or intermediate bulk containers (IBSs) turn out to be out of the scope of this test. The H2–H4 tests are very attractive because they are based on the lab-scale experiments, do not involve such a large amount of reactive product and therefore are less expensive and dangerous. At the same time all these tests have essential limitations that should be taken into account when selecting one or another test.

Detailed analysis of problems related to the SADT determination methods have been presented by Fisher [3], numerous more recent papers are focused on correctness of some particular methods (see, for instance [4–10]). This paper continues discussion of certain important aspects of the SADT determina-

tion methods. The consideration is illustrated by the abstract simulated examples that are capable of conveying the ideas without superfluous details. The numerical simulations were implemented by using the Fork and ThremEx program packages developed by CISP [11].

2. Overview of the methods for SADT determination

2.1. The United States SADT test H1

The US SADT test H1 (and the Dewar test H4) is based on the following definition of the SADT:

SADT is the lowest environment (oven) temperature at which

overheat in the middle of the specific commercial

packaging exceeds 6 °C after a lapse of the period

of 7 days (168 h) or less　　　　　　　　　(D1)

This period is measured from the time when the packaging center temperature reaches 2 °C below the oven temperature (Fig. 1a).

The US SADT test represents the series of full-scale experiments that are carried out with the specific commercial packagings of a product. The packaging is inserted in the test chamber (oven) and is maintained at a constant oven temperature. The temperature in the center of the packaging is monitored. Every experiment of the series is implemented with the new packaging. The step of the oven temperature variation is 5 °C.

According to the thermal explosion theory the essential attribute of an explosion is the critical temperature T_{CR} which, for a packaging of given size, delimits the explosive and non-explosive domains of reaction proceeding. What is the relation between the SADT based on the characteristic overheat ΔT_6, which is used as the criterion, and T_{CR}? To answer this question we considered two cases when the simple first-order reaction and the autocatalytic reaction occur in a product ($\rho = 1000$ kg/m^3; $c_p = 2000$ J/kg/K). In both the cases an explosion in the barrel of 0.6 m height and 0.2 m radius ($S = 1$ m^2, $V = 75$ L) had been simulated assuming that temperature distribution in the barrel is uniform (model of a well stirred tank, hereafter referred to as the lumped system). This model is suitable for low-viscous liquids. The initial temperature T_0 is 20 °C, boundary conditions of the 3rd kind with heat transfer coefficient $U = 4.7$ W/m^2/K were specified on all the external surfaces of the barrel. Mass of a product was 75 kg.

Table 1
Derivation of control and emergency temperatures

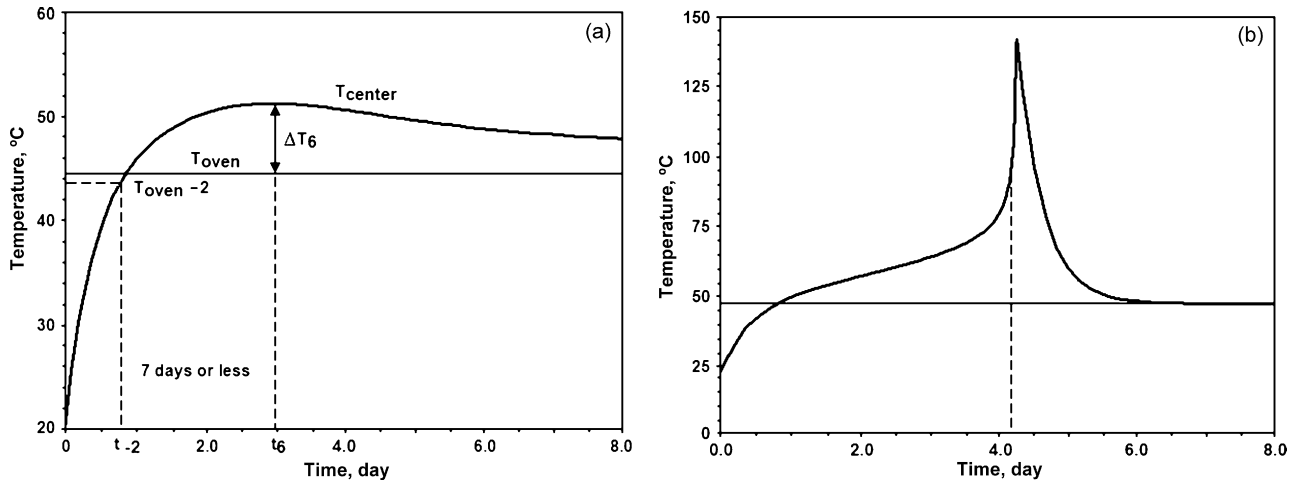| Receptacle	Group	SADT	Control t-re	Emergency t-re
	1	20 °C or less	20 °C below SADT	10 °C below SADT
Single packagings and IBSs	2	Over 20–35 °C	15 °C below SADT	10 °C below SADT
	3	Over 35 °C	10 °C below SADT	5 °C below SADT
Portable tanks	4	<50 °C	10 °C below SADT	5 °C below SADT

Fig. 1. Determining SADT along the H1 test: the first-order reaction, lumped system. (a) The ambient temperature equals SADT (H1 test) and (b) the ambient temperature equals the critical temperature of thermal explosion.

- Case 1. The first order reaction:

$$\frac{dQ}{dt} = Q^{\infty} k_0 \, e^{-E/RT}(1-\alpha); \quad k_0 = 1.19 \times 10^9 \, s^{-1};$$

$$E = 93.6 \, kJ/mol; \quad Q^{\infty} = 500 \, J/g \tag{1}$$

The SADT (Fig. 1a) equals to 44.5 °C (Fig. 1a). The temperature course of the reaction reveals that it proceeds in the non-explosive domain. ΔT_6 is reached after a lapse of ∼2.2 days. T_{CR} for the barrel (Fig. 1b) is 46.7 °C, the induction period is about 4 days.

- Case 2. The autocatalytic reaction:

$$\frac{dQ}{dt} = Q^{\infty} k_0 \, e^{-E/RT}(1-\alpha)(\alpha + z); \quad k_0 = 4.84 \times 10^9 \, s^{-1};$$

$$E = 90 \, kJ/mol; \quad Q^{\infty} = 500 \, J/g; \quad z = 0.03 \tag{2}$$

Fig. 2 depicts the results of simulation. In this case the SADT equals to 34.8 °C (Fig. 2a), ΔT_6 is reached after a lapse

of 7 days, and the explosion occurs soon after reaching ΔT_6. T_{CR} (Fig. 2b) is 31.2 °C, the induction period is about 18 days. It is obvious that at the SADT determined in accordance with definition (D1) the reaction proceeds in the explosive domain far above the criticality.

Let us now determine the SADT for a solid substance when heat transfer in it is governed by thermal conductivity (substance properties are the same as indicated above). In this case temperature distribution across the vessel is essential. The H1 test has been simulated for the same barrel by using the complete model with distributed parameters [11] (distributed system). The results simulated are presented in Table 2 together with the results for the lumped system.

The non-uniformity of a system causes quite big difference in the SADT and T_{CR} for the first-order reaction. Diminution of thermal conductivity results in lowering of the SADT and T_{CR} so that the packaging with a solid product can even pass into the group 2 (Table 1) instead of 3. The SADTs and critical temperatures for the autocatalytic reaction are less sensitive to
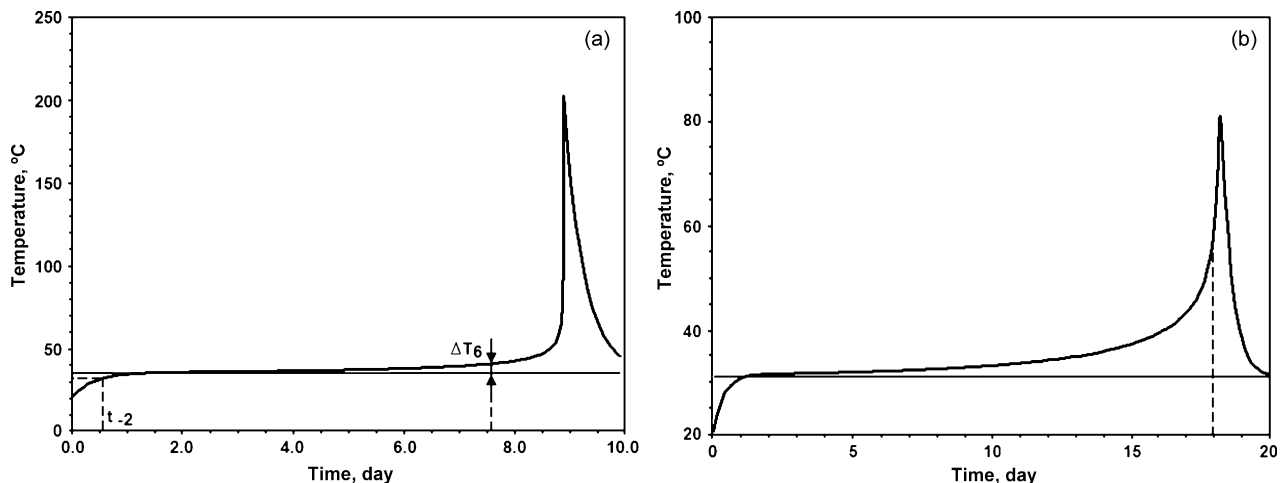

Fig. 2. Determining SADT along the H1 test: the autocatalytic reaction, lumped system. (a) The ambient temperature equals SADT (H1 test) and (b) the ambient temperature equals the critical temperature of thermal explosion.

Table 2
Comparison of SADT and T_{CR} for lumped and distributed systems

Type of the system	First-order reaction		Autocatalytic reaction	
	SADT (°C)	T_{CR} (°C)	SADT (°C)	T_{CR} (°C)
Lumped	44.5	46.7	34.8	31.2
Distributed ($\lambda = 0.6$ W/m/K)	38.7	41.6	32.7	27.2
Distributed ($\lambda = 0.1$ W/m/K)	28.5	31.4	28	20.9

change of the heat transfer mechanism and variation of thermal conductivity.

Specific feature of the autocatalytic reaction explains this fact. Namely, the initial reaction rate is very low; reaction accelerates mostly because of accumulation of the product-catalyst. During the main part of the induction period heat is evolved slowly and its amount is rather small (see [11,12] for more details). Therefore the system turns out to be closer to uniformity so that for solids with high and moderate thermal conductivity the lumped system model properly predicts the SADT. Note that this feature of the autocatalysis explains also why, in contrast to the non-self-accelerating reaction, the overheat ΔT_6 is reached just before the explosion occurs.

These examples clearly demonstrate one intrinsic peculiarity of the SADT defined in accordance with (D1) – for non-self-accelerating reaction the SADT is always below T_{CR} whereas for autocatalytic reaction the SADT can be much higher than T_{CR}. The difference between the SADT and T_{CR} depends on the reaction kinetics, but the tendency remains in force. It can be shown that the same feature is valid for complex multi-stage reactions.

The observations discussed lead to several important conclusions.

1. Mechanism of heat transfer in a substance essentially affects critical temperature irrespective of the type of a reaction. The SATD is sensitive to mechanism of heat transfer; this effect ranges from quite strong for non-self-accelerating reactions to moderate for autocatalytic reactions.
2. The SADT defined in accordance with (D1) is reasonable indicator of criticality for non-autocatalytic reactions (though it can be somewhat conservative).
3. In case of autocatalytic reactions the SADT does not give any information about critical conditions but the SADT is higher than critical temperature.

2.2. The adiabatic and isothermal storage tests H2 and H3

The H2 and H3 tests are based on the different definition of the SADT:

SADT is the critical ambient temperature rounded to the next

$\qquad$ *higher multiple of $5\,°C$* $\hfill$ (D2)

Both these tests are laboratory-scale experimental methods. The specific rate of heat generation evaluated from the corresponding calorimetric data is plotted on the Semenov diagram (Fig. 3) together with the straight line of the specific heat loss
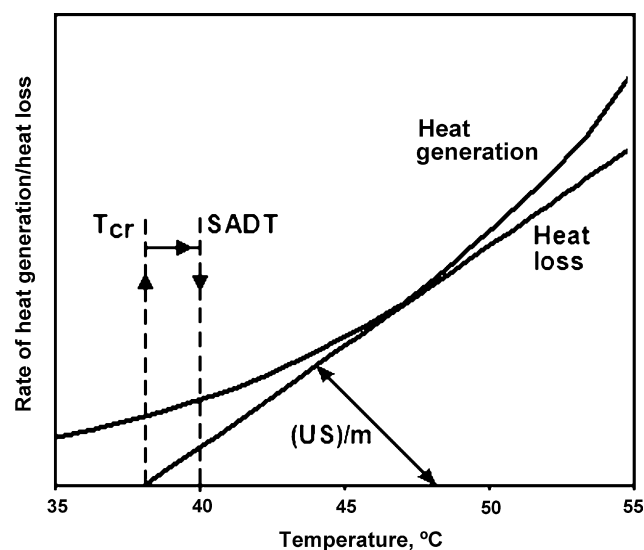

Fig. 3. Determining SADT in accordance with the H2 and H3 tests. (*US*)/*m* stands for the specific heat loss for a commercial packaging.

for a commercial packaging. Ambient temperature at which the heat loss line becomes the tangent to the heat generation curve represents critical temperature of thermal explosion.

This principle of the SADT determination implies that the H2 and H3 tests are essentially based on the lumped system model (the Semenov model of thermal explosion is valid only for a lumped system). Therefore the first limitation is that they cannot be applied for characterizing solid products.

The H2 and H3 tests differ from each other in calorimetric technique used for experimental investigation, and in the reaction types that can be assessed.

The H2 test exploits adiabatic calorimetry. The heat generation rate is evaluated from the self-heat rate data taking into account thermal inertia of the adiabatic bomb. The resultant data contain information about reactant consumption and temperature dependency of a reaction.

The H3 test is based on the use of isothermal calorimetry. Therefore series of experiments at different temperatures should be implemented to determine temperature dependency of a reaction rate. Moreover, in accordance with the test procedure the maximal rate of heat generation should be drawn on the Semenov diagram. It results in two important features.

1. In case of non-self-acceleration reaction maximal rate occurs at the very beginning of a reaction. Therefore the heat generation rate curve on the Semenov diagram will not take into

Table 3
Comparison of the SADTs calculated in accordance with H1, H2 and H3 tests

Test	First-order reaction		Autocatalytic reaction	
	SADT (°C)	T_{CR} (°C)	SADT (°C)	T_{CR} (°C)
H1	44.5	46.7	34.8	31.2
H2	45	44.8	40	37.5
H3	45	43.3	35	30.1

account the reactant consumption (as if the reaction were of zero-order) and T_{CR} evaluated from the diagram will be lower than the real critical temperature.

2. In case of autocatalytic reaction T_{CR} evaluated from the diagram will represent the correct critical temperature. As it was shown by Merzanov [12], author of the quasi-stationary theory of thermal explosion for autocatalytic reactions, the Semenov method can be applied for evaluating T_{CR} for such reactions provided that the maximal reaction rate is used instead of initial one.

This overview reveals additional limitations of the tests.

1. The H2 test cannot give reliable estimates if a reaction is autocatalytic. Moreover it is unusable for complex reactions because of the limitations of the Semenov theory.
2. The H3 test is capable of proper estimation of T_{CR} for autocatalytic reactions, but will always result in conservative estimates of T_{CR} for non-self-acceleration reactions. Applicability of this test in case of complex reaction requires special analysis.

Let us now apply the H2 and H3 tests for determining the SADT for the same two cases from pervious section. The results for the lumped system are presented in Table 3.

All the tests discussed give nearly the same SADT value for the first-order reaction. As it was predicted the Isothermal test H3 slightly underrates T_{CR}, but it does not affect the SADT estimate. In case of the autocatalytic reaction the H2 test results in the noticeably inflated values of the SADT and T_{CR}.

It should be emphasized that in case of the pronounced autocatalysis the difference in definitions of the SADT the tests H1 and H3 are based on (compare (D1) and (D2)) may result in serious inconsistency of the values. For instance, if T_{CR} determined by the H3 test for the autocatalytic reaction were just 0.2 °C lower, i.e. 29.9 °C, then the SADT would be 30 °C, which is by ~5° lower than determined by using the H1 test. Let us cite another example related to the same barrel as discussed earlier, which contains organic peroxide. Its decomposition is highly exothermic (the overall heat effect is ~2000 J/g) and is characterized by strong autocatalysis. The SADT calculated according to the H1 test is 51 °C, $T_{CR} = 32.5$ °C. The H3 test gives precisely the same value of T_{CR} so that the SADT = 35 °C. The H1 test suggests that for this peroxide assignment of control temperature is not required (the SADT > 50 °C) whereas the H3 test results indicate that the product should be attributed to Group 2 (Table 1)!

2.3. The heat accumulation storage test H4

The H4 test is based on the same SADT definition (D1) as the H1 test and the same procedure is used for determination. The main difference is that the small Dewar vessel (up to 1 L) filled with the tested substance is used for experiments instead of a commercial packaging. Therefore some scale-up of the results on the full-size packaging is required. This is the key problem of the test.

2.3.1. TDG scale-up procedure

The TDG suggests that the SADT determined by using the H4 test will be representative for a commercial packaging or IBS if the specific heat loss (in W/kg/K) is the same for the Dewar vessel and the packaging:

$$\left(\frac{US}{V}\right)_P = \left(\frac{US}{V}\right)_D, \tag{3}$$

where indices P and D denote packaging and Dewar, respectively.

This condition is easily derived from the heat balance equation for the lumped system.

The important and very useful practical feature of the scale-up condition (3) (and of the Semenov theory in general) is that it does not depend on the specific geometry of a vessel but only on the ratio of the surface of a vessel to its volume.

The TDG also suggests determining specific heat loss by measuring half-cooling time $t_{1/2}$ for a packaging:

$$\frac{US}{V} = \rho c_p \frac{\ln 2}{t_{1/2}} \tag{4}$$

This scaling method is valid only for a well-stirred tank and, strictly speaking, the H4 test can be applied only for low-viscous liquids because in this case the temperature distribution in the Dewar vessel and in a packaging is approximately uniform.

Applicability of the H4 test for determining the SADT for solids, when internal heat transfer is governed by thermal conductivity, is perhaps the most disputable issue related to the SADT (see, for instance, recent publications [6–10]) because of the complexity of the scale-up problem. Therefore we will consider it in more detail.

Just as the scale-up method for liquids is based on the Semenov theory the scale-up for solids must be derived from the Frank-Kamenetskii theory (we deliberately consider only the simplest theories). Unfortunately there are several factors that hamper direct application of this theory.

1. The theory had been created assuming that temperature on the surface of a solid body is defined (boundary conditions of the first kind). Contrary to it heat losses along the Newtonian law are typical for transportation or storage conditions (boundary conditions of the third kind).
2. This stationary theory does not consider development of a process in time whereas the SADT involves time

(approximate of explosion induction period) as the essential parameter.

3. The theory gives analytical relations that are mostly applicable to the bodies of the simplest shapes—sphere, infinite cylinder and infinite slab. Many practical shapes such as barrel or box remain above its range.

2.3.2. Scale-up based on similarities between Semenov and Frank-Kamenetskii theories

For the first time the possibility to apply the results of the Semenov theory for approximate analysis of thermal explosion development in solid bodies of simple shapes was demonstrated by Frank-Kamenetskii [13]. Based on the formal similarity of the critical conditions for the lumped and the distributed system

$$\frac{E}{RT_0^2}Qk_0\,e^{-E/RT_0} = \frac{1}{e}\frac{US}{V}; \qquad \underbrace{\frac{E}{RT_0^2}Qk_0\,e^{-E/RT_0} = \frac{\lambda}{r^2}\delta_{cr}}_{\text{distributed system}}$$

lumped system

(5)

Frank-Kamenetskii derived that the results of the Semenov theory can be approximately applied to solid bodies of simple shapes if to use the effective value of the heat transfer coefficient:

$$U_0 = \frac{V}{Sr^2}\lambda e\delta_{cr} \qquad (6)$$

where r denotes the characteristic size (radius for a sphere or cylinder, half-thickness of an infinite slab).

Grewer [14] proposed to apply this idea for scaling-up the results of H4 test on the commercial packaging. Specifically he showed that the Dewar test performed for a self-reactive powder in a 500 cm³ Dewar flask with $U_0 \approx 0.33$ W/m²/K will be representative for a spherical packaging with $r = 0.27$ m calculated from (6) at $\delta_{cr} = 3.32$, which corresponds to the volume of about 80 L (see also [8]).

Unfortunately there are several principal arguments against this scale-up method.

As a matter of fact the very similarity between the critical conditions for the lumped and the distributed systems (5) is purely formal and does not have solid physical grounds. Nevertheless the concept of an effective heat transfer (6) can be used for rough estimates of explosion development in a solid but only under conditions of the first kind. It is quite evident from the expression (6), which does not contain real heat losses but characterizes only internal heat transfer governed by thermal conductivity. For instance, Grewer's results correspond to a packaging with Biot criterion Bi > 30. Barzikin and Merzhanov [15] showed that the Frank-Kamenetskii stationary theory becomes valid for Bi > 10 so that the H4 test from the example cited by Grewer is in fact representative for a packaging well under boundary conditions of the first kind.

The boundary problem of the explosion theory (an explosion under condition of Newtonian heat exchange with environment) had been considered in detail in [15]. Authors proposed more general approximate expression for effective value of the heat transfer coefficient U_{eff} that takes into account both internal heat transfer and external heat exchange U:

$$U_{eff} = \frac{UU_0}{U + U_0}, \qquad U_0 = \frac{V}{Sr^2}\lambda e\delta_{cr} \qquad (7)$$

Bowes [16] showed that by substituting this effective coefficient in the condition (3) instead of the real value of U one can achieve more reliable scaling-up of the H4 test results. Nevertheless this scale-up method is still applicable only to simple forms and, hence, does not allow correct estimation of the SADT for many practical cases. Moreover, it is principally inapplicable if a complex exothermic reaction proceeds in a product (including autocatalytic reactions) because neither Semenov nor Frank-Kamenetskii theory covers such cases.

2.3.3. Scale-up based on the theory of regular cooling mode

One can propose more universal scale-up method based on providing thermal equivalence of solid bodies of different size and even of different shapes having different physical properties. The theoretical ground of the method is the concept of regular cooling mode introduced by Kondratiev [17].

Let us consider temperature variation in inert solid bodies of simple shapes (sphere, slab, infinite and finite cylinder, parallelepiped) heated in an environment with constant temperature T_e (boundary conditions of the third kind). Temperature in any point of a body is represented by the infinite series [18]

$$\frac{T - T_e}{T_0 - T_e} = \sum_{n=1}^{\infty}\prod_{i=1}^{3}A_{n,i}X_{n,i}\exp\left(-\frac{\mu_{n,i}^2}{r_i^2}\,at\right). \qquad (8)$$

Here $A_{n,i}$ stand for initial thermal amplitudes that depend on initial temperature distribution and body shape, $X_{n,i}$ are geometry-dependent functions, r_i denote characteristic dimensions of a body, $\mu_{n,i}$ are the roots of the characteristic equations, they are complex tabular functions of Bi: $\mu_{n,i} = \mu_{n,i}(\text{Bi}_i)$, $\text{Bi}_i = Ur_i/\lambda$. After a lapse of the transient period t_r only the first term of the series (8) remains significant and the regular mode of cooling is set in:

$$\frac{T - T_e}{T_0 - T_e} = \prod_{i=1}^{3}A_{1,i}X_{1,i}\exp\left(-\frac{\mu_{1,i}^2}{r_i^2}\,at\right). \qquad (9)$$

or, in the differential form

$$\frac{\partial(T - T_e)}{\partial\tau} = -\omega(T - T_e), \qquad \frac{\partial\ln(T - T_e)}{\partial\tau} = -\omega;$$

$$\omega = a\sum_{i=1}^{3}\frac{\mu_{1,i}^2}{r_i^2} \qquad (10)$$

where ω is the cooling tempo and $\mu_{1,i}$ is the first roots of the corresponding characteristic equations.

The regular cooling (or heating) mode is distinguished by several important features.

1. At the expiration of the transient period the logarithmic rate of temperature variation in any point of a solid body of

any shape regardless of the initial temperature distribution becomes identical and constant.

2. The cooling tempo ω depends on heat transfer coefficient (through $\mu_1(\mathrm{Bi})$) and on thermal diffusivity of a substance. Thus ω represents an integral characteristic that gives proper weight of external heat exchange and internal conductive heat transfer within a solid substance.

3. Matching the cooling tempos for vessels of different shape and size having different physical properties ensures equivalence of their thermal behavior. Specifically, a Dewar flask and a commercial packaging will be equivalent if

$$\omega_D = \omega_P. \tag{11}$$

Strictly speaking this condition of thermal equivalence is valid only for inert systems. For a self-reacting substance only approximate equivalence can be observed provided that heat generation due to an exothermic reaction is small and deviation of a reactive system form the inert one is also small. Usually this requirement is fulfilled during the most part of the induction period especially in the vicinity of criticality. In particular this is the case when the SADT is to be determined because the overheating does not exceed 6 °C.

The scale-up method based on regular cooling mode (hereafter referred to as the RCM method) has several essential advantages.

1. The cooling tempo can be easily calculated from (10) for bodies of different shapes if thermal–physical properties of a substance and external heat transfer coefficient are known.

For simple shapes (sphere, infinite cylinder and infinite slab) (10) is reduced to the formula

$$\omega = a \left[\frac{\mu_1(\mathrm{Bi})}{r} \right]^2 \tag{12a}$$

where r is the characteristic dimension (radius for a sphere or cylinder and half-thickness for a slab); the function $\mu_1(\mathrm{Bi})$ in tabular form can be found in [18,19] (see also Appendix A).

As it follows from (10) cooling tempos for bodies of more complex shapes are calculated on the basis of the superposition principle. Thus, a finite cylinder (barrel) can be interpreted as the intersection of an infinite cylinder and slab, therefore

$$\omega = a \left[\frac{\mu_{1s}^2}{(h/2)^2} + \frac{\mu_{1c}^2}{r^2} \right]; \qquad \mathrm{Bi_s} = \frac{U_s h/2}{\lambda};$$

$$\mathrm{Bi_c} = \frac{U_c r}{\lambda}, \tag{12b}$$

where indices s and c denote slab and cylinder respectively, μ_{1s} and μ_{1c} represent the first roots of the characteristic equations for infinite slab and infinite cylinder, r radius of a cylinder and h is its height.
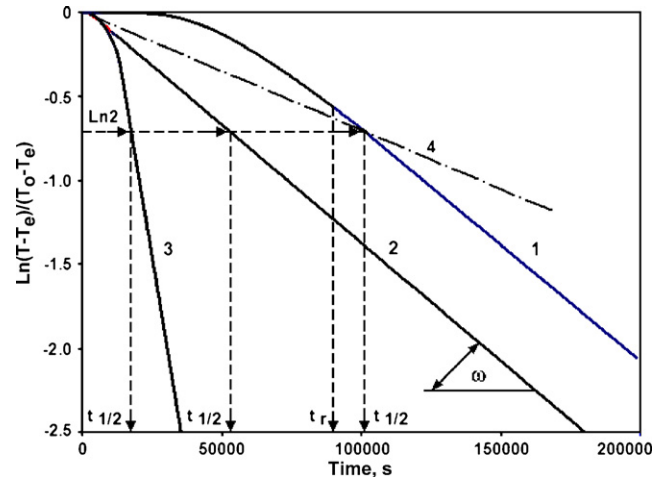

Fig. 4. Cooling of spherical vessels: (1) $r = 25$ cm; (2) $r = 5$ cm; (3) $r = 15$ cm; (4) a small vessel has the same $t_{1/2}$ as a large one; $T_0 = 80$ °C, $T_e = 20$ °C, $U_1 = U_3 = 10$ W/m²/K; $U_2 = 0.456$ W/m²/K.

A parallelepiped is the intersection of three infinite slabs, therefore

$$\omega = a \sum_{i=1}^{3} \left(\frac{\mu_{1s}(\mathrm{Bi}_{si})}{h_i/2} \right)^2; \qquad \mathrm{Bi}_{si} = \frac{U_{si} h_i/2}{\lambda}, \tag{12c}$$

where h_1, h_2 and h_3 represent dimensions of a parallelepiped.

2. The cooling tempo can be determined experimentally by using an inert solid substance or a reactive substance at temperatures where a reaction is negligibly slow.

Fig. 4 depicts typical cooling curves for spherical vessels of different size with a solid substance ($c_p = 2000$ J/kg/K, $\rho = 1000$ kg/m³, $\lambda = 0.2$ W/m/K). Curves 1 and 2 represent cooling of the thermally equivalent vessels of significantly different size, the equality of ω is provided by selecting the appropriate values of heat transfer coefficient ($U = 10$ W/m²/K for the large vessel as against $U = 0.456$ W/m²/K for the small one). Curve 3 demonstrates significant increase of ω for a vessel of a medium size with the same specific heat transfer US/V as for the large one (in both the cases $US/V = 120$ W/m³/K so that for the medium vessel $U = 6$ W/m²/K). Note that for the small vessel, which is thermally equivalent to the large vessel $US/V = 27.4$ W/m³/K.

Fig. 4 vividly illustrates the complete inapplicability of the concept of the specific heat transfer to solids emphasized by Fierz [6]. In case of a packaging with a solid both internal heat transfer governed by thermal conductivity and external heat losses from the surface are of key importance. Contributions of these mechanisms essentially depend on thermal diffusivity of a substance, heat transfer coefficient, and geometry and dimensions of a package. From this point of view results of packaging calibration cannot be transferred on the same packaging containing any other solid substance with different physical properties. It is in contrast with TDG recommendation to use dicyclohexyl phthalate as a calibration substance.

Furthermore, transient period that precedes the regular mode goes up significantly with increase of a packaging size

Table 4
The SADTs for thermally equivalent spherical Dewar and packaging

Reaction type	US test H1 (packaging)	Heat accumulation storage test H4, different scale-up methods			
		RCM (ω = const.) [$U_D = 0.452^a$]	$t_{1/2}$ = const. [$U_D = 0.24^a$]	Bowes ($U_{eff}S/V$ = const.) [$U_D = 0.4^a$]	TDG (US/V = const.) [$U_D = 2^a$]
N-order	33.6	35.9	30.3	34.5	48.4
Autocatalytic	30.3	31.7	29.8	31.3	36.9

[a] Measured in W/m²/K.

and can be comparable or even longer than half-cooling time (compare curves 1 and 2 in Fig. 4). It can lead to some confusing results. Thus, the small vessel would have the same half-cooling time as the large one (curve 4, Fig. 4) if U were 0.24 W/m²/K, i.e. U would be almost two times smaller than it is required for thermal equivalence. It demonstrates once more that the half-cooling time cannot be used as a proper indicator of thermal equivalence.

3. The fact that the cooling tempo measured experimentally has well defined physical meaning allows applying various ways of a vessel calibration.

A cooling experiment can be performed by using some inert solid substance with physical properties different form those of a reacting product. Then U is calculated by using one of the formulas (12a)–(12c) with the following calculation of ω for the solid product under interest.

In the same way the results of calibration of a commercial packaging allow calculation of U_D for a Dewar flask that will ensure thermal equivalence and vice versa.

The following examples illustrate these possibilities and will allow several useful conclusions.

Example 1 The cooling tempo $\omega = 2.67 \times 10^{-5}\,\text{s}^{-1}$ has been determined (simulated in our case) for the commercial spherical packaging ($r = 0.25\,\text{m}$) containing a solid product ($c_p = 1000\,\text{J/kg/K}$, $\rho = 1000\,\text{kg/m}^3$; $\lambda = 0.2\,\text{W/m/K}$; $a = 2 \times 10^{-7}\,\text{m}^2/\text{s}$).

(a) In accordance with (12a) $\mu_{1,P} = r_P\sqrt{\omega/a} = 0.25\sqrt{2.67 \times 10^{-5}/2 \times 10^{-7}} = 2.89$. This value corresponds to $Bi_P = U \times r_P/\lambda = 12.5$ (column A1 of Appendix A) hence $U_P = Bi_P \times \lambda/r_P = 12.5 \times 0.2/0.25 = = 10\,\text{W/m}^2/\text{K}$ for the packaging.

(b) Now we can calculate U_D for the spherical Dewar with $r_D = 0.05\,\text{m}$ filled with the same substance. The cooling tempo for the Dewar must be the same as for the packaging, therefore $\mu_{1,D} = r_D\sqrt{\omega/a} = 0.05\sqrt{2.67 \times 10^{-5}/2 \times 10^{-7}} = 0.578$. From column A1 we get $Bi_D = 0.113$ so that $U_D = Bi_D \times \lambda/r_D = 0.113 \times 0.2/0.05 = 0.452\,\text{W/m}^2/\text{K}$. The SADT determined for the Dewar flask and the packaging are presented in Table 4. It demonstrates also the SADTs determined for the same spherical Dewar flask on the basis of other scale-up methods.

One can see that the RCM scale-up method ensures reasonable correspondence between the SADTs determined though the

H4 test gives somewhat overstated values. In case of an autocatalytic reaction the results are less sensitive to the approximate nature of scaling.

Scale-up based on equality of half-cooling times also allows obtaining reasonable estimates but on a conservative side. The origin of this conservatism has been discussed earlier (see Fig. 4). Important note is that this scale-up method will give such results only provided that half-cooling times were determined experimentally for a packaging and for a Dewar flask.

Table 4 demonstrates that estimates provided by the Bowes method are in good accord with the results of the RCM method. Nevertheless one should avoid using this method for autocatalytic and, all the more, complex multi stage reactions.

Finally, the TDG method demonstrates total inadequacy.

Example 2 represents more complex case of a real Dewar flask with round bottom described in [10] (see Fig. 5a) with different heat loses on different surfaces, specifically $U_{top} = 3.5\,\text{W/m}^2/\text{K}$ whereas $U_{side} = U_{bottom} = 0.29\,\text{W/m}^2/\text{K}$. The flask is filled with a solid reactive substance ($\rho = 464\,\text{kg/m}^3$, $\lambda = 0.16\,\text{W/m/K}$, $c_p = 1450\,\text{J/kg/K}$). The inner flask is supposed to be made of stainless steel: wall thickness is 1 mm, $\rho = 7000\,\text{kg/m}^3$, $\lambda = 16\,\text{W/m/K}$, $c_p = 500\,\text{J/kg/K}$. The effective thermal inertia of the Dewar is 1.37, i.e. the same as indicated in [10].

(a) Thermal behavior of this object has been simulated numerically. The pronounced temperature distribution along the symmetry axis appears in the course of cooling. Fig. 5b depicts variation of relative temperature in three different points—near the top (curve 1), in the middle (curve 2) and
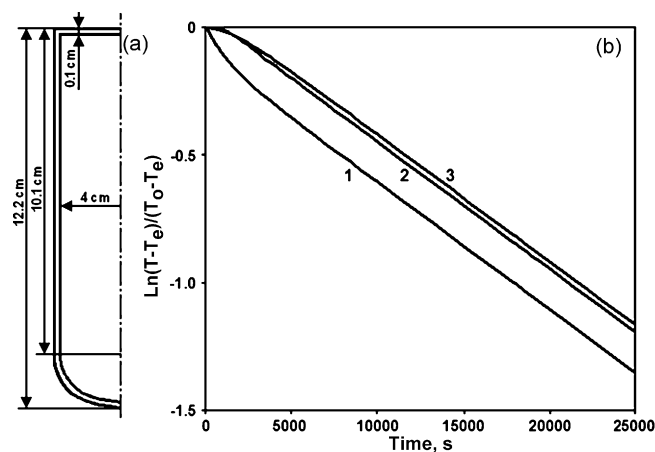

Fig. 5. Cooling of the Dewar flask. (a) Sketch of the inner flask and (b) temperature variation in different locations: (1) 1 cm from the top, (2) the middle and (3) 1 cm from the bottom.

Table 5
The SADTs for thermally equivalent Dewar and barrels

Vessel	SADT (°C)	
	First-order reaction	Autocatalytic reaction
Shelled Dewar, $r = 0.04$ m	47	36.5
Barrel, $r = 0.18$ m ($U = 8.6$ W/m^2/K)	42	34.4
Barrel, $r = 0.145$ m ($U = 3$ W/m^2/K)	42.7	34.7

close to the bottom (curve 3). After a lapse of the transient period the regular cooling mode is set and the cooling tempo in all the points becomes the same: $\omega = 4.97 \times 10^{-5}$ s^{-1}.

(b) Now one can calculate the parameters of a barrel (commercial packaging) that will be represented by this Dewar flask. Under the assumption that $h_P = 2r_P$ and that heat losses are the same on all the surfaces formula (13b) gives: $\omega = a(\mu_{1s}^2 + \mu_{1c}^2)/r^2$; $Bi_s = Bi_c = U_p \times r/\lambda$. The packaging contains the same solid substance so that $a = 2.38 \times 10^{-7}$ m^2/s. There are two unknown parameters—radius r_P and the heat transfer coefficient U_P therefore one can estimate U_P for a barrel of given size or calculate the size for the given U_P.

1. The barrel size is assigned: $r_P = 0.18$ m (volume of the barrel is ~36 L). The appropriate values of the first roots should be found in columns A2 and A3 (Appendix A). They must correspond to the same value of Bi and the sum of their squires must be equal to $\omega r^2/a = 6.76$. The sought for values correspond to Bi = 9.71: $\mu_{1s} = 1.43$ and $\mu_{1c} = 2.17$. Finally the required value of U_p is 8.6 W/m^2/K.

   It should be emphasized that the correlation between packaging size and intensity of heat exchange is very strong. Thus, for a barrel of radius $r_P = 0.2$ m (volume is ~50 L) Bi will be more than 100, i.e. the barrel proves to be under the conditions of the first kind.

2. It is known that $U_p = 3$ W/m^2/K. In this case determination of the appropriate values of μ_{1s} and μ_{1c} requires several iterations: first, Bi is calculated for some initial guess on r, then values of μ_{1s} and μ_{1c} are evaluated, cooling tempo ω_P is calculated and compared with ω_D. If $\omega_P \neq \omega_D$ the next iteration is implemented with the changed value of r. In our case the resultant values of the first roots are $\mu_{1s} = 1.16$, $\mu_{1c} = 1.74$, and radius of the barrel is 0.145 m (Bi = 2.72).

Table 5 represents the calculated SADTs for the Dewar flask and the equivalent barrels.

As in the previous cases the resultant SADTs for the autocatalytic reaction are close enough to each other and no significant sensitivity to the approximate nature of the scale-up method is observed. Contrary to it difference between the SADTs for the Dewar and the barrels for the N-order reaction reaches about 5 °C and prediction by the H4 test is on the unsafe side.

The effect of the flask wall explains this discrepancy. A thin highly conductive metallic wall has very low thermal resistance, reaction heat is transferred from a substance through a wall almost instantly and dissipated by the outer wall surface, which is larger than the proper surface of a substance. As the wall

is thin the increment in the heat loss surface is small. Therefore its effect on thermal mode is negligible if the system is far from criticality—either in explosive or in non-explosive domain (including an inert system). It means that no significant effect of the wall will be observed when cooling experiment or the SADT determination for the autocatalytic reaction because the SADT is higher than the critical temperature.

Contrary to this, if the conditions are close to critical (which is the case for non-self-acceleration reaction at the SADT) even very small variation of parameters governing heat balance (surface of heat loss is one of them) may seriously affect the resultant thermal mode.

The following data illustrate the discussion.

1. Cooling simulation of the Dewar flask with and without shell results in almost the same cooling tempos: $\omega = 4.97 \times 10^{-5}$ s^{-1} for the shelled Dewar and $\omega = 5.02 \times 10^{-5}$ s^{-1} for the substance without a shell (idealized Dewar). The actual inner size of the flask was used for simulation of the idealized Dewar.

2. The SADT for the idealized Dewar (with the same heat losses as in Example 2) equals to 44 °C for the N-order reaction and 35.5 °C for the autocatalytic one. In the first case discrepancy between the SADTs for the Dewar and the equivalent barrels lessened by 3 °C, in the second case—by 1 °C.

3. We determined the effective heat transfer coefficient on the side and the bottom of the idealized Dewar (keeping the same $U_{top} = 3.5$ W/m^2/K) that provides the same SADT as for the shelled Dewar. It proved out to be 0.5 W/m^2/K instead of 0.29 W/m^2/K—about 1.7 times larger.

This specific effect of a wall rapidly subsides along with increase of Bi (either due to increase of U or because of growth of the vessel size) so that for the barrels considered the SADTs remain practically unchanged regardless of whether a thin shell is added or not.

Another important observation is that the effect of shell heat capacity on the thermal mode is very weak. Thus, 500 times reduction of the heat capacity changes the SADT by ~0.3 °C.

We could see (Table 4) that three different scale-up methods resulted in obtaining comparable estimates. Additional analysis reveals features of the methods and helps to choose one or another of methods.

Limitation of the RCM method is that cooling tempo cannot be calculated analytically for such complex objects as the real Dewar (complex geometry or different and asymmetrical heat losses on different surfaces). In these cases the RCM method allows only one-way scale-up—from a Dewar to a packaging, therefore the cooling tempo for a Dewar should be determined experimentally. The use of numerical simulation allows applying the RCM method in full measure to complex systems.

The Bowes method is useful but has several serious limitations. Two of them have been mentioned already—inapplicability in case of complex geometry or reaction mechanism. Another limitation is that it cannot be applied if heat losses are asymmetrical. Moreover, detailed knowledge about thermal properties of a system is required, in particular heat transfer

coefficient should be known for a packaging or a Dewar. As it was shown, this parameter can be reliably evaluated only from cooling tempo after its determination.

The scale-up based on equality of half-cooling times can provide reasonable and even conservative estimates if this equality has been provided by direct measurement of $t_{1/2}$ for every specific substance, Dewar and packaging. Important problem is that, because this method is purely empirical when it concerns solids, it is impossible to predict how variation of geometry, physical properties and features of a reaction can affect reliability of the results.

Summarizing all these facts one can conclude that the RCM method, having better justified physical basis, has better prospects, especially in combination with methods of mathematical simulation.

Important practical observation is that in all the cases irrespective of the scale-up method applied it appeared that the ~400 mL Dewar flask, depending on its geometry and geometry of a package, can be reasonably representative for a packaging with the volume of about 30–40 L. Determination of the SADT for solid-containing packages of larger volume by using the H4 test is impossible.

The last note of this section concerns the reason why the results of the SATD determination for many organic peroxides by using the H4 and H1 tests are in good agreement (see statement in [8–10]). We believe that the main reason is in autocatalytic decomposition mechanism, which is typical for organic peroxides. We could see that in this case due to specific feature of self-accelerating reactions different methods for the SADT determination give very comparable results. It is also very likely that more correct half-cooling time scale-up method has been used, i.e. $t_{1/2}$ was measured for the Dewar and a packaging.

3. Applying the kinetics-based simulation for SADT determination

Overview of the tests recommended by the TDG for determining the SADT reveal numerous problems that can be met while applying one or another method.

The H1 test is very time and cost consuming and cannot be used for big packages or tanks.

The H2 an H3 tests are rather flexible and cost-effective but they are principally inapplicable for solid products. In addition they are based on different definition of the SATD, which can lead to getting the results that are incomparable with the results of other methods.

The H4 test is also time consuming and is fraught with various problems when it concerns investigation of solid substances. Moreover this test cannot predict properly the SADTs for big packages or tanks.

In these circumstances the kinetics-based simulation approach can be very beneficial addition to the tests. It comprises three main steps:

- implementing necessary series of calorimetric experiments;

Table 6
SADT and critical temperature for a box and for a stack of boxes

Container	Single box		Stack of boxes	
	SADT (°C)	T_{CR} (°C)	SADT (°C)	T_{CR} (°C)
Metallic	57	61	48	54
Polymer	55	57	39	42

- creating the mathematical model of a reaction on the basis of experimental data;
- incorporating the kinetic model into the model of a process and achieving the practical target by using mathematical (numerical) simulation.

The detailed discussion of the approach is out of the scope of this paper; it can be found in [20]. Here we will mention only that it can help in those very cases when the experimental methods for the SADT determination are either inapplicable at all or turn out to be troublesome or problematic.

One could see the advantages of applying the kinetics-based simulation method for analysis of various scenarios presented in previous sections—all the illustrative results were simulated.

The following example demonstrates how this method helps in solving the problem when neither of experimental methods is applicable. It concerns determination of the SADT for the stack of boxes. In accordance with TDG the SADT should be determined for a commercial package subject to transport. However it is usual practice to transport packaged goods in stacks rather than to carry every single packaging separately. Apparently the SADT for a stack will differ form those for a single package. It is also obvious that this parameter cannot be estimated by either of the experimental tests.

Let us compare the shelled box of $20\,cm \times 20\,cm \times 20\,cm$ size containing 7.5 kg of reactive solid product and the stack of 27 ($3 \times 3 \times 3$) boxes. The product decomposes along the single-stage first order reaction with $E = 110\,kJ/mol$, $k_0 = 1.96 \times 10^{11}\,s^{-1}$, $Q^\infty = 500\,J/g$.

The container wall thickness is 2 mm. We will consider two cases—metallic container ($\lambda = 16\,W/m/K$) and container made of polymer ($\lambda = 0.2\,W/m/K$). In both these cases thermal conductivity of a product was the same: $\lambda = 0.15\,W/m/K$.

The simulated results (Table 6) demonstrate that the SADT for the single box is much higher than those for the stack and even exceeds its critical temperature so that the use of this SATD for the stack will be absolutely unsafe. Thus, for boxes with polymer containers, the induction period of the stack explosion at ambient temperature 55 °C is 4.5 days, i.e. smaller than the permissible 7 days.

The remarkable detail of the results obtained is that significant difference between the SATDs and critical temperatures for the stacked-up boxes with metallic and polymer containers is observed whereas single boxes with different container materials behave similarly. Analysis of the temperature fields in the stacks (Fig. 6) gives the detailed explanation.

If containers are of metal the walls, though thin enough, serve as very efficient heat conducting elements. At the heating stage
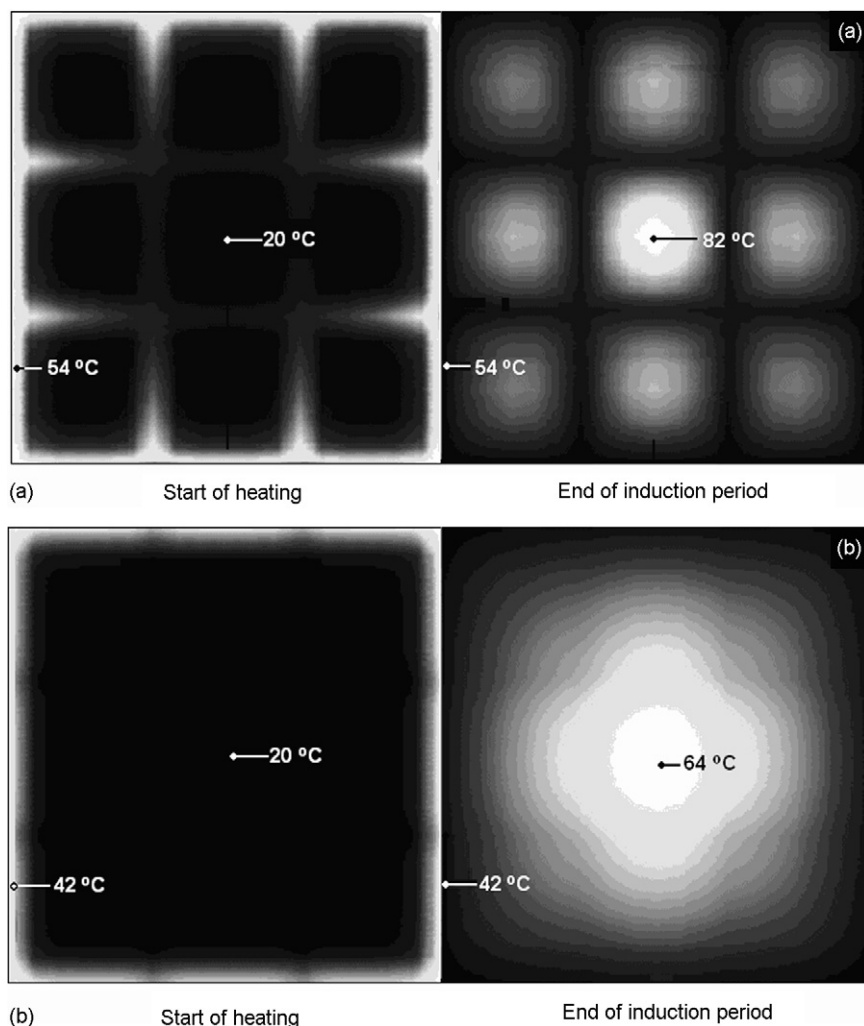
Fig. 6. Temperature distribution in the stack cross-section. (a) Stack of boxes with metallic containers and (b) stack of boxes with polymer containers.

they facilitate external heat to penetrate into a stack (Fig. 6a, left drawing) thus accelerating the heating. On the contrary, when reaction heat release becomes significant metallic walls help to withdraw heat from a stack outwards (Fig. 6a, right drawing), which leads to elevation of the SADT and critical temperature.

The polymer has about the same thermal conductivity as the reactant therefore the stack behaves almost as a monolithic box of the reactant of the same size as the stack so that both the SADT and critical temperature are much lower than for the single small box (Fig. 6b).

4. Conclusions

1. The principal limitation of the adiabatic and isothermal storage tests H2 and H3 is that they are unfit for determination of the SADT for solid products. Furthermore, the H2 test is fraught with obtaining erroneous and, more important, unsafe estimates of the SADT if an autocatalytic reaction proceeds in a product. Therefore it should not be applied in such cases.
2. The H2 and H3 tests are based on different definition of the SADT as against the H1 and H4 tests. This difference can

result in obtaining inconsistent estimates of the SADT for the same package. To avoid such kind of misleading it is highly desirable to use one definition for any of methods intended for the SADT assessment. As long as no new universal definition is proposed one can recommend to apply the definition based on permissible overheat (the H1 and H4 tests) which ensures reasonable estimates both for non-self-accelerating and autocatalytic reactions.

3. The heat accumulation storage (Dewar) H4 test can be considered as restrictedly applicable for determining the SADT for solid products provided that the adequate scale-up method has been selected. In particular, the 400 mL Dewar flask can be representative for packages of up to approximately 30 L. It was shown that the half-cooling time method can give reasonable results if this time interval is measured directly both for the flask and for a packaging. The Bowes method can be applied for simple determinations (simple geometry and kinetics).
4. The RCM method proposed in the paper represents the advanced, more universal approach to scaling though it requires use of mathematical simulation in complex cases.

It was also demonstrated that this method provides the most correct determination of thermal physical properties of a vessel. Nevertheless it should be emphasized that all the scale-up methods are approximate ones and do not guaranty real thermal equivalence of reactive systems of different sizes and geometries.

5. Kinetics-based simulation approach is the general method for SADT determination. In some cases (complex geometry, complex reactions, SADT for stack of packages or bulked cargos, etc.) numerical simulation is the only way to get answers. Therefore it can be proposed as very useful and promising additional method.

All the demonstrated results have been obtained by using the software developed by Cheminform St. Petersburg, Ltd. Specifically the Fork program was used for simulation of lumped systems and the ThermEx package—for simulation of processes in solids (distributed systems) and automatic SADT determination in compliance with the US SADT test.

Fig. A1. Dependency of the first roots on Bi. ($\blacksquare$), ($\bullet$) and ($\blacktriangle$) tabular values and (—) polynomial approximation.

Appendix A. First roots of the characteristic equations

Bi	μ_1		
	Sphere (A1) tg $\mu = -\mu/(Bi-1)$	Slab (A2) ctg $\mu = \mu/Bi$	Cylinder (A3) $J_0(\mu)/J_1(\mu) = \mu/(Bi-1)$
0.02	0.24450	0.141	0.1995
0.04	0.34500	0.1987	0.2814
0.06	0.42170	0.2425	0.3438
0.08	0.48600	0.2791	0.396
0.1	0.54230	0.3111	0.4417
0.2	0.75930	0.4328	0.617
0.4	1.05280	0.5932	0.8516
0.6	1.26140	0.7051	1.0184
0.8	1.43200	0.791	1.149
1	1.57080	0.8603	1.2558
1.5	1.83660	0.9882	1.4569
2	2.02880	1.0769	1.5994
3	2.28890	1.1925	1.7887
4	2.45570	1.2646	1.9081
5	2.57040	1.3138	1.9898
6	2.65370	1.3496	2.049
7	2.71650	1.3766	2.0937
8	2.76540	1.3978	2.1286
9	2.80440	1.4149	2.1566
10	2.83630	1.4289	2.1795
15	2.93200	1.4729	2.2509
20	2.98750	1.4961	2.288
30	3.03700	1.5202	2.3261
50	3.07880	1.54	2.3572

Polynomial approximation of the dependency $\mu_1(Bi)$: $\mu_1 = a_0 + \sum_{1}^{4} a_i X^i; \; X = \sqrt{Bi}$ (13)

a_0	−0.0736	−0.0288	−0.0529
a_1	2.1513	1.2059	1.7423
a_2	0.5748	−0.3724	−0.501
a_3	0.0689	0.0518	0.0651
a_4	−0.0031	−0.0027	−0.0031
R^2	0.9997	0.9998	0.9998

The polynomial (13) provides sufficient precision of approximation (correlation coefficients for all the geometries are very close to 1) and can simplify calculations required when using the RCM method.

Fig. A1 illustrates dependency of $\mu_1(Bi)$ and quality of polynomial approximation.

References

[1] Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 4 revised ed., United Nations, ST/SG/AC.10/11/Rev. 4, United Nations, New York and Geneva, 2003.

[2] Globally Harmonized System of Classification and Labelling of Chemicals (GHS), United Nations, New York and Geneva, 2003.

[3] H.G. Fisher, D.D. Goetz, Determination of self-accelerating decomposition temperature for self-reactive substances, J. Loss Prev. Process Ind. 6 (3) (1993) 183–194.

[4] Y. Li, K. Hasegava, On the thermal decomposition mechanism of self-reactive materials and the evaluating method for their SADTs, in: Proceedings of the Ninth International Symposium on Loss Prevention and Safety Promotion in Process Industries, Barcelona, Spain, May 4–8, 1998.

[5] J. Sun, Y. Li, K. Hasegava, A study of self-accelerating decomposition temperature (SADT) using reaction calorimetry, J. Loss Prev. Process Ind. 14 (5) (2001) 331–336.

[6] H. Fierz, Influence of heat transport mechanisms on transport classification by SADT-measurement as measured by the Dewar-method, J. Hazard. Mater. 96 (2–3) (2003) 121–126.

[7] H. Fierz, Comments on the Letter to the Editor from M. Malow, U. Krause, K.D. Wehrstedt, J. Hazard. Mater. 103 (2003) 175–177.

[8] M. Malow, U. Krause, K.-D. Wehrstedt, Letter to the Editor. Some comments on the paper of H. Fierz, J. Hazard. Mater. 103 (2003) 169–173.

[9] M. Steensmaa, P. Schuurman, M. Malow, U. Krause, K.-D. Wehrstedt, Evaluation of the validity of the UN SADT H.4 test for solid organic peroxides and self-reactive substances, J. Hazard. Mater. V 177 (2–3) (2005) 89–102.

[10] M. Steensma, P. Schuurman, Determination of SADT of solids by United Nations Heat Accumulation Storage Test, in: Proceedings of the Third NRIFD Symposium, Tokyo, Japan, March 10–12, The National Research institute of Fire and Disaster, 2004, pp. 104–115.

[11] A. Kossoy, I. Sheinman, Evaluating thermal explosion hazard by using kinetics-based simulation approach, Process Safety Environ. Protect. Trans. IchemE 82 (2004) 421–430 (B6 Special Issue: Risk Management).

[12] A.G. Merzanov, F.I. Dubovitski, Quasi-stationary theory of thermal explosion of self-accelerating reactions, J. Phys. Chem. 34 (10) (1960) 2235–2243 (in Russian).

[13] D.A. Frank-Kamenetskii, Diffusion and Heat Exchange in Chemical Kinetics, 2nd ed., Plenum Press, New York, 1969.

[14] T. Grewer, Thermal Hazards of Chemical Reactions, Industrial Safety Series, Elsevier, Amsterdam, 1994.

[15] V.V. Barzikin, A.G. Merzhanov, Boundary-value problem in the theory of thermal explosion, Dokl. AN SSSR 20 (1958) 1271–1276 (in Russian).

[16] P.C. Bowes, Notes on the Wormestau-Lagerung Test, Working Party on Organic Peroxides, Berlin, 1975.

[17] G.M. Kondratiev, Regular Thermal Mode, Gostechisdat, Moscow, 1954 (in Russian).

[18] A.V. Likov, Theory of Thermal Conductivity, Visshaja Shkola, Moscow, 1967 (in Russian).

[19] W.M. Rohsenow, J.P. Hartnett, Y.I. Cho, Handbook of Heat Transfer, 3rd ed., Mc-Graw-Hill Publishing, New York, 1998.

[20] A. Kossoy, A. Benin, Yu. Akhmetshin, From experimental data via kinetic model to predicting reactivity and assessing reaction hazards, in: Proceedings of the Mary Kay O'Connor Process Safety Center 2001 Annual Symposium "Beyond Regulatory Compliance, Making Safety Second Nature", College Station, TX, USA, 2001.