

**Committee of Experts on the Transport of Dangerous Goods  
and on the Globally Harmonized System of Classification  
and Labelling of Chemicals**

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**Sub-Committee of Experts on the  
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Item 2 (c) of the provisional agenda

**Explosives and related matters: review of tests in  
parts I, II and III of the Manual of Tests and  
Criteria**

**Sub-Committee of Experts on the Globally Harmonized  
System of Classification and Labelling of Chemicals**

**Thirty-eight session**

Geneva, 11-13 December 2019

Item 2 (a) of the provisional agenda

**Classification criteria and related hazard  
communication: Work of the Sub-Committee of  
Experts on the Transport of Dangerous Goods (TDG)  
on matters of interest to the GHS Sub-Committee**

**Manual of Tests and Criteria, update test Series H:  
determination of self-accelerating decomposition  
temperature**

**Transmitted by the Chairman of the Working Group on Explosives**

1. This information paper contains the outcome of the work of International Group of Experts on the Unstable and Energetic Substances (IGUS), working group Energetic and Oxidizing Substances (EOS), ad-hoc working group on revision of UN test series H.
2. The Working Group of Explosives for a couple of years worked on the improvements of the test descriptions of the Manual of Tests and Criteria. The outcome of this work is given in document ST/SG/AC.10/46/Add.2.
3. UN Test series H, was discussed in the working group of explosives briefly. Only the polymerizing substances and the Self-Accelerating Polymerization Temperature (SAPT) were incorporated as well as the adaption of text where there was a need to make the Manual of Test and Criteria fit for both transport and GHS.
4. In parallel, for a couple of years, an IGUS-EOS ad-hoc working group discussed the update of UN test series H. The following aspects were discussed:
  - The update of the current test descriptions and delete over-specification;
  - On test series H.2: Adiabatic Storage Test (AST): to make the test description and description of the equipment to be used more general and the introduction of pressure adiabatic storage test (closed system);
  - On test series H.3: Isothermal Storage Test (IST) to make the test description and description of the equipment to be used more general;
  - The introduction of standard heat-loss values, where possible (otherwise to be determined for the specific configuration), for packaging's and IBCs;
5. The outcome of the discussions and consequent proposed amendments to the **7<sup>th</sup> revised edition of the manual of tests and criteria** are given in this document. All changes are indicated; inserted text is shown **red** and deleted text in **red, strikethrough**.

6. Both sub-committees are invited to comment on the current proposal, either during the sessions or intersessionally by correspondence.
7. The intention is to include all comments before the next session in a formal proposal to both sub-committees. Commenters are therefore kindly asked to take the deadline for formal proposals into account when submitting their comments.

## “SECTION 28 TEST SERIES H

### 28.1 Introduction

This test series contains test methods for the determination of the self-accelerating decomposition temperature (SADT) and the self-accelerating polymerization temperature (SAPT). The SADT is defined as the lowest temperature at which self-accelerating decomposition may occur with a substance in the packaging. The SAPT is defined as the lowest temperature at which self-accelerating polymerization may occur with a substance in the packaging. The SADT and SAPT are measures of the combined effect of the ambient temperature, reaction kinetics, package size and the heat transfer properties of the substance and its packaging. To assist in interpreting the results, ~~the following models can be used in which the main resistance to heat flow is:~~

- ~~\_\_\_\_\_ (a) At the boundary i.e. packaging (Semenov model);~~
  - ~~\_\_\_\_\_ (b) Within the substance (Frank-Kamenetskii model); or~~
  - ~~\_\_\_\_\_ (c) A combination of these (Thomas model).~~
- (a) Semenov model, in which the main resistance to heat flow is at the boundary (i.e. packaging). This model is generally applicable to homogeneous liquids but can also be applied to solids in packagings (excluding IBC<sup>2</sup>s);
  - (b) Frank-Kamenetskii model, in which the main resistance to heat flow is within the substance. This model is generally applicable to solids in larger packagings, IBCs or tanks;
  - (c) Thomas model, in which the resistance to heat flow is from both the boundary and the substance;
  - (d) Non-stationary models, e.g. finite element methods (FEM), or computational fluid dynamics (CFD) all combined with thermal kinetic methods.

The text should be used in conjunction with the temperature control requirements given in sub-section 2.5.3.4 of the Model Regulations.

*Both the SADT and the SAPT may be influenced by factors such as aging of the sample, presence of stabilizers or impurities in the sample (including packaging materials in contact with the substance). These possible influencing factors should be considered when evaluating the results of an SADT or SAPT determination.*

**References:** N.N. Semenov, *Z. Physik*, 48, 1928, 571.  
D.A. Frank-Kamenetskii, *Zhur. Fiz. Khim.*, 13, 1939, 738.  
P.H. Thomas, *Trans. Faraday Soc.*, 54, 1958, 60.

## 28.2 Test methods

28.2.1 Test series H comprises tests and criteria concerning the thermal stability of substances at transport temperatures or concerning the determination of whether a substance meets the definition of a self-reactive substance or a polymerizing substance.

28.2.2 Each test involves either storage at a fixed external temperature and observation of any reaction initiated or storage under near adiabatic conditions and measurement of the rate of heat generation versus temperature. The test methods included in test series H are given in Table 28.1. Each of the methods listed is applicable to solids, liquids, pastes and dispersions.

**Table 28.1: Test methods for test series H**

Test code	Name of test	Section
H.1	United States SADT test <sup>a</sup>	28.4.1
H.2	Adiabatic storage test (AST) <sup>b</sup>	28.4.2
H.3	Isothermal storage test (IST) <sup>b</sup>	28.4.3
H.4	Heat accumulation storage test <sup>c</sup>	28.4.4

<sup>a</sup> Recommended test for substances transported in packagings.

<sup>b</sup> Recommended test for substances transported in packagings, IBCs or tanks.

<sup>c</sup> Recommended test for substances transported in packagings, IBCs or small tanks.

The list of tests is not exhaustive; other tests may be used provided that they give the correct SADT or SAPT of the substance as packaged.

28.2.3 When temperature control is necessary (see Table 28.2) the control and emergency temperatures should be derived from the SADT or SAPT using Table 28.3.

**Table 28.2: Criteria for temperature control**

Type of substance	Criterion for temperature control
Self-reactive substance	SADT ≤ 55 °C
Organic peroxide Type B and C	SADT ≤ 50 °C
Organic peroxide Type D showing medium effect when heated under confinement <sup>a</sup>	SADT ≤ 50 °C
Organic peroxides Type D showing low or no effect when heated under confinement <sup>a</sup>	SADT ≤ 45 °C
Organic peroxides Type E and F	SADT ≤ 45 °C
Polymerizing substance in packaging or IBC	SAPT ≤ 50 °C
Polymerizing substance in portable tank	SAPT ≤ 45 °C

<sup>a</sup> As determined by test series E as prescribed in this Manual of Tests and Criteria, Part II.

**Table 28.3: Derivation of control and emergency temperatures**

Type of receptacle	SADT/SAPT <sup>a</sup>	Control temperature	Emergency temperature
Single packagings and IBCs	≤ 20 °C	20 °C below SADT/SAPT	10 °C below SADT/SAPT
	over 20 °C to 35 °C	15 °C below SADT/SAPT	10 °C below SADT/SAPT
	over 35 °C	10 °C below SADT/SAPT	5 °C below SADT/SAPT
Portable tanks	≤ 45 °C	10 °C below SADT/SAPT	5 °C below SADT/SAPT

<sup>a</sup> *i.e. the SADT/SAPT of the substance as packaged.*

28.2.4 If a substance is being tested to determine whether it is a self-reactive substance, a test of series H, or a suitable alternative test, should be performed to determine if its SADT would be less than or equal to 75 °C when transported in a 50 kg package.

28.2.5 If a substance is being tested to determine whether it is a polymerizing substance, a test of series H, or a suitable alternative test, should be performed to determine if its SAPT would be less than or equal to 75 °C in its packaging, IBC or portable tank.

28.2.6 The results obtained for ~~the largest commercial~~ packages are applicable to smaller packages of similar construction and material provided that the heat transfer per unit mass is no smaller than from the larger package.

### 28.3 Test conditions

28.3.1 For organic peroxides and self-reactive substances the preliminary procedure (see section 20.3) should be performed and the effect of heating under confinement (test series E) determined before performing SADT tests. *Safety precautions should be taken which allow for the possibility of catastrophic failure of the test vessel and for the hazards arising from the ignition of secondary fuel-air mixtures and the evolution of toxic decomposition products. Substances liable to detonate should only be tested with special precautions.*

28.3.2 The test selected should be conducted in a manner which is representative, both in size and material, of the package. For metal packagings, IBCs or tanks, it may be necessary to include a representative amount of the metal in the sample tested i.e. representative of both the metal(s) and the area of contact.

28.3.3 *Extra care should be taken when handling samples which have been tested since changes may have occurred rendering the substance more unstable and more sensitive. Tested samples should be destroyed as soon as possible after the test.*

28.3.4 Samples which have been tested at a particular temperature and are apparently unreacted may be used again, for screening purposes only, provided extra care is taken. Fresh samples should be used for the ~~final actual~~ determination of the SADT or SAPT.

28.3.5 If the complete package is not tested, the heat loss data used for the determination of the SADT or SAPT should be representative of the package, IBC or tank. ~~For all type of packagings up to 50 kg for solids or 200 kg/225 litres for liquids and for IBCs up to 1250 litres for liquids, a standard heat loss per unit of mass is given in Table 28.4. For other packagings, IBC's or tanks or when there is a need for a heat loss value that deviates from the one as given in Table 28.4, the actual heat loss value per unit of mass has to be determined. In this case, the~~ heat loss per unit of mass of the package, IBC or tank may be determined by calculation (taking account of the quantity of substance, dimensions of the package, heat transfer in the substance, ~~and~~ the

heat transfer through the packaging and heat transfer from the outer wall of the packaging to the environment\*) or by measuring the half-time of cooling of the package filled with the substance or another substance having similar physical properties. The heat loss per unit mass,  $L$  (W/kg.K), can be calculated from the half-time of cooling,  $t_{1/2}$  (s), and the specific heat,  $C_p$  (J/kg.K), of the substance using the formula:

$$L = \ln 2 \times \left( \frac{C_p}{t_{1/2}} \right)$$

\* For calculations an external heat transfer coefficient (i.e. heat transfer from the outer wall of the packaging to the environment) of  $5 \text{ W/m}^2.\text{K}$  can be used

28.3.6 The half-time of cooling can be determined by measuring the period of time in which the temperature difference between the sample and its surroundings is decreased by a factor of 2. For example, for liquids, the packaging may be filled with silicone oil, apparent density  $0.96 \pm 0.02$  at  $20 \text{ }^\circ\text{C}$  and heat capacity  $1.46 \pm 0.02 \text{ J/g}$  at  $25 \text{ }^\circ\text{C}$  or dimethyl phthalate and this heated to about  $80 \text{ }^\circ\text{C}$ . Water should not be used as erratic results may be obtained through evaporation/condensation. For solids for example, the packaging may be filled with dense soda ash (apparent density greater than  $1 \text{ g/cm}^3$ ) and this is heated to about  $80 \text{ }^\circ\text{C}$ . The temperature drop is measured at the centre of the package over the temperature range which includes the expected SADT or SAPT. For scaling, it may be necessary continuously to monitor the temperature of the substance and surroundings and then use linear regression to obtain the coefficients of the equation:

$$\ln \{T - T_a\} = c_o + c \times t$$

where:  $T$  = substance temperature ( $^\circ\text{C}$ );  
 $T_a$  = ambient temperature ( $^\circ\text{C}$ );  
 $c_o$  =  $\ln\{\text{Initial substance temperature} - \text{initial ambient temperature}\}$ ; and  
 $c$  =  $L/C_p$ ;  
 $t$  = time (s).

28.3.7 Standard ~~Examples of the~~ heat loss characteristics of ~~some typical~~ packages, IBCs and tanks are given in Table 28.34. The actual value obtained will depend on the shape, wall thickness, surface coating etc. of the packaging.

**Table 28.3: HEAT LOSS PER UNIT MASS FROM PACKAGES, IBCs AND TANKS**

Type of receptacle	Normal capacity (litres)	Filling	Heat loss per unit mass (L) (mW/K.kg)
<i>For liquids:</i>			
1A1	50	47.5 kg-DMP <sup>a</sup>	63
1H1	50	47.5 kg-DMP <sup>a</sup>	94
1H1	200	200 kg-water	56
3H1 (black)	60	47.5 kg-DMP <sup>a</sup>	105
6HG2	30	35.0 kg-DMP <sup>a</sup>	69
IBC 31-HA1	500	500 kg-water	51
Tank	3-400	3-400 kg-water	18 <sup>b</sup>
Tank container (insulated)	20-000	14-150 kg-isododecane	1.7

*For solids:*

1G	38	28.0 kg DCHP <sup>e</sup>	35
1G	50	37.0 kg DCHP <sup>e</sup>	29
1G	110	85.0 kg DCHP <sup>e</sup>	22
4G	50	32.0 kg DCHP <sup>e</sup>	27

<sup>a</sup> — *DMP = dimethyl phthalate.*

<sup>b</sup> — *Calculated using a heat transfer coefficient of 5 W/m<sup>2</sup>.K.*

<sup>e</sup> — *Dicyclohexyl phthalate (solid).*

**Table 28.4: HEAT LOSS PER UNIT MASS FROM PACKAGES, IBCs AND TANKS**

Type of receptacle	Normal capacity (litres)	Heat loss per unit mass (L) (mW/K.kg) <sup>b</sup>
<i>For liquids:</i>		
Packagings	up to 200 kg/225 l	40 <sup>a</sup>
Packagings	larger than 200 kg/225 l	no standard value <sup>c</sup>
IBCs	up to 1250 l	30
IBCs	larger than 1250 l	no standard value <sup>c</sup>
Tanks		no standard value <sup>c</sup>
<i>For solids:</i>		
Packagings	up to 50kg	30 <sup>a</sup>
Packagings	larger than 50 kg	no standard value <sup>c</sup>
IBCs	-	no standard value <sup>c</sup>
Tanks	-	no standard value <sup>c</sup>

<sup>a</sup> 60 mW/K.kg for liquids and 30 mW/K.kg for solids to be used for 50 kg packaging when used for classification purposes.

<sup>b</sup> For test series H.4 the heat loss of the Dewar vessel to be used should be as close as possible to the value listed in the table.

<sup>c</sup> Value should be determined for the actual configuration

## 28.4 Series H test prescriptions

### 28.4.1 Test H.1: United States SADT test

#### 28.4.1.1 Introduction

This method determines the minimum constant temperature air environment at which self-accelerating decomposition or polymerization occurs for a substance in a specific package. Packages of up to 225 litres may be tested by this method. An indication of the explosion hazard from the decomposition or polymerization reaction can also be obtained.

#### 28.4.1.2 Apparatus and materials

28.4.1.2.1 The test substance and packaging should be representative of that intended for commercial use. The packaging forms an essential part of the test.

28.4.1.2.2 The apparatus consists of a test chamber in which the air surrounding the package under test can be maintained at a constant temperature for a period of at least ten days.

28.4.1.2.3 The test chamber should be constructed such that:

- (a) It is well insulated;
- (b) Thermostatically controlled air circulation is provided so as to maintain a uniform air temperature within  $\pm 2$  °C of the desired temperature; and
- (c) The minimum separation distance for all sides from the package to the wall is 100 mm.

Any type of oven may be used provided that it is capable of meeting the temperature control requirements and will not ignite any decomposition products. Examples of a suitable small-package and large-package ovens are described below, given in 28.4.1.2.4 and 28.4.1.2.5 respectively.

#### Example 1

28.4.1.2.4 — A small-package oven may be constructed from an open head 220 litre steel drum. This will readily accommodate packages of up to 25 litres capacity. Construction details are shown in Figure 28.4.1.1. Larger packages may be tested as long as a 100 mm clearance between the package and the oven wall is maintained.

#### Example 2

28.4.1.2.5 — An expendable large-package oven may be made from 50 mm × 100 mm lumber formed into a cubic frame 1.2 m on each side, which is lined inside and out with 6 mm thick waterproof plywood and insulated all around with 100 mm fibreglass insulation. Construction details are shown in Figure 28.4.1.2. The frame should be hinged on one side to permit loading and unloading of test drums. The floor should be provided with 50 mm × 100 mm lumber on edge, spaced 200 mm on centres to keep the test container off the floor and allow free air circulation around the package. Cleats should run normal to the door to permit a fork-lift to move the drums. A circulating fan should be located on the side opposite the door. The air flow should be from the upper corner of oven to the fan discharge at the diagonally opposite lower corner. An electric heater of 2.5 kW is suitable for heating the air. Thermocouples should be placed in the air intake and outflow ducts as well as



the top, middle and bottom of the oven. For substances with an SADT or SAPT below ambient temperature, the test should be performed in a cooling chamber or solid carbon dioxide should be used for cooling the oven.

#### Example 3

For tests at temperatures up to 75 °C, a double walled metal chamber (minimum separation distance from the package to the wall is 100 mm) may be used with fluid from a temperature-controlled circulating bath passed between the walls at the desired temperature. The test chamber is loosely closed by an insulated lid (e.g. made from 10 mm thick polyvinyl chloride). The temperature control should allow the desired temperature for a liquid inert sample to be maintained with a deviation of not more than  $\pm 2$  K for up to 10 days.

28.4.1.2.64 The package should be equipped with a thermowell which positions the thermocouple or Resistance Temperature Detector (RTD) at the package mid-point. The thermowell may be constructed of glass, stainless steel or other suitable material but should be introduced in a manner which does not reduce package strength or venting capability.

28.4.1.2.75 Continuous temperature-measuring and recording equipment, which is protected from fire and explosion hazards, is required.

28.4.1.2.86 *The tests should be performed in an area which provides adequate protection from fire and explosion hazards, and from toxic fumes. A safety distance, e.g. 90 m, from public roads and occupied buildings is recommended. If there may be toxic fumes, longer safety distances may be required.*

#### 28.4.1.3 Procedure

28.4.1.3.1 The package is weighed. A thermocouple or RTD is inserted in the package to be tested such that the temperature in the centre of the sample can be monitored. If the required oven temperature is below ambient, the oven is switched on and the inside of the oven cooled to the desired temperature before placing the package in the oven. If the required oven temperature is at or above ambient temperature, the package is inserted in the oven at ambient temperature and the oven then switched on. There should be a minimum clearance of 100 mm between the package and the sides of the oven.

28.4.1.3.2 The sample is heated and the temperature of the sample and test chamber continuously monitored. The time is noted at which the sample temperature reaches a temperature 2 °C below the test chamber temperature. The test is then continued for a further seven days or until the sample temperature rises to 6 °C or more above the test chamber temperature if this occurs sooner. ~~Note the time taken for the sample to rise from the 2 °C below the test chamber temperature to its maximum temperature.~~

28.4.1.3.3 When the test is completed, cool the sample and remove it from the test chamber. Note the variation of temperature with time. If the package remains intact, note the percentage mass loss and determine any changes in composition. Dispose of the sample as soon as possible.

28.4.1.3.4 If the temperature of the sample does not exceed the oven temperature by 6 °C or more then repeat the test with a new sample in an oven at a 5 °C higher temperature. The SADT or SAPT is defined as the lowest oven temperature at which the sample temperature exceeds the oven temperature by 6 °C or more. If the substance is being tested to determine if temperature control is necessary, perform sufficient tests to determine the SADT or SAPT to the nearest 5 °C or to determine if the SADT or SAPT is greater than ~~the applicable temperature specified in Table 28.2. or equal to 60 °C.~~ If the substance is being tested to determine if it meets the SADT criterion for a self-reactive substance, perform sufficient tests to determine if the SADT for a 50 kg package is 75 °C or less. If the substance is being tested to determine if it meets the SAPT criterion

for a polymerizing substance, perform sufficient tests to determine if the SAPT in the packaging as used is 75 °C or less.

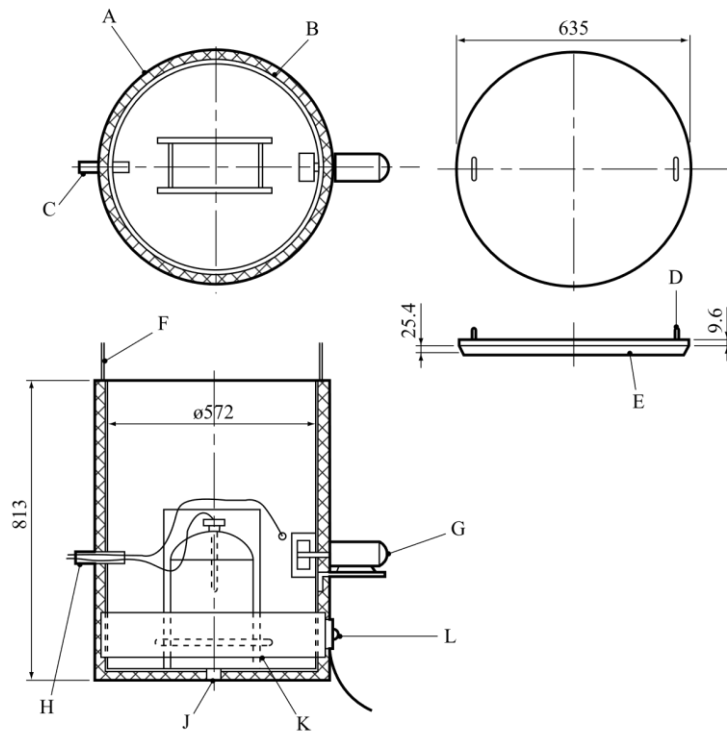
28.4.1.4 *Test criteria and method of assessing results*

28.4.1.4.1 The SADT or SAPT is reported as the lowest temperature at which the sample exceeds the oven temperature by 6 °C or more. If the sample temperature does not exceed the oven temperature by 6 °C or more in any test, the SADT or SAPT is recorded as being greater than the highest oven temperature used.

28.4.1.5 *Examples of results*

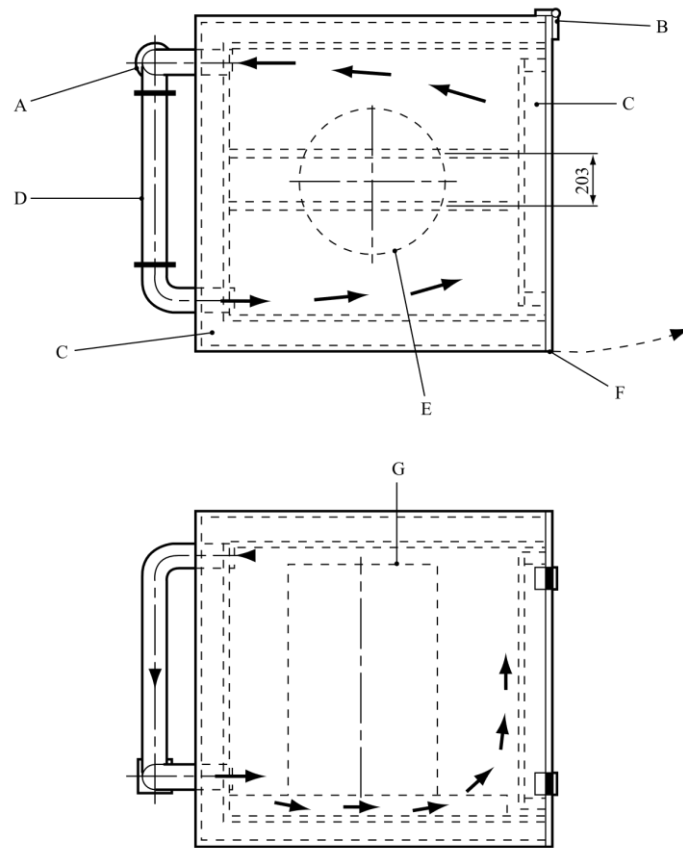
Substance	Sample mass (kg)	Packaging	SADT/SAPT (°C)
tert-Amyl peroxybenzoate	18.2	6HG2, 22.8 litres	65
tert-Butyl peroxyacetate (60%)	7.2	6HG2, 22.8 litres	75
Dibenzoyl peroxide	0.45	1G	70
Di-(4-tert-butylcyclohexyl) peroxydicarbonate	43	1G	40
2,5-Diethoxy-4-morpholinobenzene-diazonium zinc chloride (66%)	30	1G, 50 litres	50
2-(N-ethoxycarbonyl-N-phenylamino)-3-methoxy-4-(N-methyl-N-cyclohexylamino)benzenediazonium zinc chloride (62 %)	10	6HG1, 25 litres	50
Didecanoylperoxide, technically pure	20	1G	40
2,2'-Azodi-(isobutyronitrile)	50	1G	50

Figure 28.4.1.1: Small package oven (Example 1)



- 
- |                               |                                    |
|-------------------------------|------------------------------------|
| (A) Insulation 25 mm thick    | (B) 220 litres open top drum       |
| (C) 19 mm pipe                | (D) 9.6 mm eye bolt in steel cover |
| (E) Insulation on steel cover | (F) 3 mm control cable             |
| (G) Fan                       | (H) Thermocouples and controls     |
| (J) Drain                     | (K) 25 mm angle stand              |
| (L) 2 kW drum heater          |                                    |
-

Figure 28.4.1.2: Large package oven (top view and side view) (Example 2)



- 
- |                                 |                |
|---------------------------------|----------------|
| (A) Fan                         | (B) Hinges (2) |
| (C) Insulation                  | (D) Heater     |
| (E) Drum                        | (F) Latch      |
| (G) Drum (e.g. 0.58 m x 0.89 m) |                |
-

## 28.4.2 *Test H.2: Adiabatic storage test*

### 28.4.2.1 *Introduction*

28.4.2.1.1 This test method determines the rate of heat generation produced by a reacting substance as a function of temperature. The heat generation parameters obtained are used with the heat loss data ~~relating of~~ ~~to~~ the package to determine the SADT or SAPT of a substance in its packaging. The method is appropriate for every type of packaging, including IBCs and tanks.

There are two versions of the adiabatic storage test:

- Open version: A Dewar vessel within an oven is used for this version. This set-up uses a capillary to prevent pressure build-up and a cooling system to limit the temperature increase due to a thermal runaway reaction.
- Closed system: In this version a test vessel (e.g. Dewar or thin-walled vessel) is placed within an autoclave in an oven. Here the autoclave prevents the release of pressure to the surroundings during the test.
- 

28.4.2.1.2 ~~Measurements can be performed in the temperature range from -20 °C to 220 °C.~~ The smallest temperature rise that can be detected with this method depends on the properties of the sample, but generally corresponds to a ~~rate of~~ heat generation rate of 15 mW/kg. The upper limit of the open version is determined by the capacity of the cooling system to safely cool the substance (up to 500 W/kg if water is used as ~~the~~ coolant). ~~The closed version can disregard this limit if performed in a high pressure autoclave. Although the test is not perfectly adiabatic, the heat losses are less than 10 mW.~~ The maximum allowable error in heat generation is 30% at 15 mW/kg and 10% from 100 mW/kg to 10 W/kg. The detection limit of the adiabatic test should be suitable for assessing the heat loss from the package under consideration (e.g. 100 to 500 mW/kg for L=60 mW/kg K). If significant extrapolation of heat production rates derived from adiabatic test data is required, a validation with additional isothermal tests is recommended.

28.4.2.1.3 ~~An explosion may occur in the open version of the test if~~ the cooling system is activated at a stage where the rate of heat generation exceeds the cooling capacity of the apparatus ~~an explosion may occur.~~ For the closed version an explosion could lead to a rupture of the autoclave or its fittings. *The test site should therefore be carefully selected to reduce to a minimum the possible hazards from an explosion and of a possible subsequent gas explosion of the decomposition products (secondary explosion).*

### 28.4.2.2 *Apparatus and materials*

#### 28.4.2.2.1

##### Open version:

The apparatus consists of a glass Dewar vessel (~~max. 31.0 or 1.5~~ litre) to contain the sample, an insulated oven with a differential control system to keep the temperature in the oven to within 0.1 °C of the sample temperature, and an inert lid for the Dewar vessel. In special cases, sample holders of other construction materials may have to be used. An inert heating coil and cooling tube pass through the lid into the sample. Pressure build-up in the Dewar vessel is prevented by ~~a 2-m-long PTFE~~ sufficiently long capillary tube ~~made of an inert substance (e.g. 2 m long PTFE tube) which passes~~ through the insulated lid. A constant power heating unit is used for internal heating of the substance to a ~~pre-set~~ preset temperature or for calibration. Internal heating and cooling may be stopped or started automatically at ~~pre-set~~ preset temperatures. In addition to the cooling system, a secondary safety device is ~~used to fitted which~~ disconnects the power supply to the

oven at a ~~pre-set~~ preset temperature. A schematic drawing of ~~the~~ an open apparatus for the adiabatic storage test ~~AST~~ is given in Figure 28.4.2.1.

Closed version:

The apparatus consists of a suitable inert vessel (e.g. Dewar or thin-walled test cell) to contain the sample, a high-pressure autoclave and an insulated oven with a differential temperature control system. Thin-walled test cells require the use of a pressure control system to balance the internal and external cell pressure.

The phi-factor (heat capacity of the set-up and the sample divided by heat capacity of the sample) of the system should be known and be considered in evaluating the tests results. Therefore, a suitable combination of phi-factor, insulation, and amount of substance should be chosen. The heat losses from the apparatus and detection limit of the system also have to be taken into consideration. An inert heating coil may be inserted into the sample. In addition to the high-pressure autoclave, a secondary safety device is used to disconnect the power supply to the oven at a preset temperature.

The closed version of the test is preferred for substances with a high vapour pressure at the test temperature to prevent mass loss due to evaporation. Nevertheless, the weight of the sample should be determined after the measurement to detect mass loss during the test. Leakage from the system and the resulting evaporation cooling can result in a significant loss of sensitivity in the test and a large margin of error in the results.

28.4.2.2.2 The temperature of the substance is measured at its centre by means of thermocouples or platinum resistance sensors (RTD) placed in a steel or glass tube. The temperature of the surroundings ~~air~~ is measured at the same height as the sample temperature, also with thermocouples or platinum resistance sensors. Continuous temperature measuring and recording equipment is required to monitor the temperature of ~~the~~ substance as well as ~~and~~ (the air) in the oven. This equipment should be protected from fire and explosion. For substances with an SADT or SAPT below ambient temperature, the test should be performed ~~with sufficient cooling in a cooling chamber or solid carbon dioxide should be used for cooling the oven.~~

28.4.2.3 *Procedure*

28.4.2.3.1 ~~Calibration~~ Validation procedures

The ~~calibration~~ validation procedure ~~A~~ is as follows:

- (a) Fill the Dewar vessel with a suitable inorganic salt, preferably with similar physical properties to the test substance (e.g. sodium chloride or dense soda ash). Alternatively, an oil of known specific heat capacity at the temperature of interest (e.g. silicone oil, apparent density  $0.96 \pm 0.02$  at 20 °C and heat capacity  $1.46 \pm 0.02$  J/g at 25 °C) may be used ~~or another suitable oil and place it in the vessel holder of the AST oven;~~
- (b) Place the Dewar vessel in the vessel holder of the ~~AST~~ oven and ~~h~~Heat the ~~sample~~ ~~calibration~~ validation substance in 20 °C steps using the internal heating system at a known power rating, e.g. 0.333 W or 1.000 W, and determine the heat losses at 40 °C, 60 °C, 80 °C and 100 °C;
- (c) Use the data to determine the heat capacity of the Dewar vessel ~~and the test set-up~~ using the method given in 28.4.2.4.

The validation procedure ~~B~~ is as follows:

- (a) In order to perform validation procedure B the test set-up should be well characterized (e.g. by performing validation procedure A first);
- (b) The test set-up must be validated using the method described in section 28.4.2.4 with at least two standard substances or mixtures. Suitable choices for these standards are dicumylperoxide in ethylbenzene<sup>1</sup> (40:60% w/w, SADT for a heat loss of 60 mW/kg K should be 90 °C), or any of the substances from the example of results tables in chapter 28.

<sup>1</sup> Reference: Dürrstein S., Kappler C., Neuhaus I., Malow M., Michael-Schulz H., Gödde M., 2016, *Modell-based prediction of the adiabatic induction period and SADT of dicumyl peroxide solution and comparison to large-scale experiments performed using 216.5-liter barrels in the H.1 test*, *Chemical Engineering Transactions*, 48, 475-480.

#### 28.4.2.3.2 Test procedure

The test may be performed using an open or a closed system. The closed version of the test is strongly recommended for highly volatile liquids (to prevent mass loss through evaporation), or samples that decompose with severe pressure rises (e.g. which could throw off the insulated lid or eject the sample from the test cell in the open version of the test). The suitability of a test run in the open version can be evaluated by determining the mass loss of the sample after the test.

The test procedure is as follows:

- (a) Fill the Dewar vessel/test cell with the weighed sample, including a representative amount of packaging material (if ~~metal~~necessary), and place it in the vessel holder of the ~~AST~~oven;
- (b) Start the temperature monitoring and then increase the sample temperature ~~using the internal heater~~ to a ~~pre-set~~preset temperature at which detectable self-heating may occur. The specific heat of the substance can ~~either~~ be calculated from the temperature rise, heating time and heating power, ~~or be determined by any suitable calorimetric test method beforehand~~;
- (c) ~~Stop the internal heating~~Heat the sample to the set temperature, maintain the oven temperature and monitor the sample temperature. If no temperature rise due to self-heating is observed ~~within 24 hours~~after temperature equilibration of the system (e.g. 24 h for the open system), increase the oven temperature by 5 °C. Repeat this procedure until self-heating is detected;

For the closed version: The apparatus can be heated with <0.5 W/kg until self-heating is detected. The heating power per unit mass should remain below the sensitivity for self-heating detection of the test equipment or autoclave;

- (d) When self-heating is detected, the sample is allowed to heat up under adiabatic conditions to a ~~pre-set~~preset temperature, ~~where the rate of heat generation is less than the cooling capacity, upon~~ at which point the cooling system is activated or the oven temperature has reached its limit;

For the open version this temperature should be set so that the rate of heat generation does not exceed the cooling capacity of the system;

For the closed version this temperature is usually a preset maximum oven temperature. The sample may exceed this temperature under non-adiabatic conditions.

~~(e) — On cooling, determine the loss in mass, if any, and determine the change in composition (if desired).~~

#### 28.4.2.4 *Test criteria and method of assessing results*

28.4.2.4.1 Calculate the rate of temperature drop, A (°C/h), of the Dewar vessel at the different temperatures used in the calibration procedure. Plot a graph through these values in order to allow determination of the rate of temperature drop at any temperature.

28.4.2.4.2 Calculate the heat capacity, H (J/°C), of the Dewar vessel using the formula:

$$H = \frac{3600 \times E_1}{A + B} - (M_1 \times Cp_1)$$

where:

$E_1$	=	power applied to the internal heater (W)
A	=	rate of temperature drop at the temperature of calculation (°C/h)
B	=	slope of the curve on internal heating ( <del>calibration</del> validation substance) at the temperature of calculation (°C/h)
$M_1$	=	mass of <del>calibration</del> validation substance (kg)
$Cp_1$	=	specific heat of <del>calibration</del> validation substance (J/kg.°C)

28.4.2.4.3 Determine the heat loss, K (W), using:

$$K = \frac{A \times (H + M_1 \times Cp_1)}{3600}$$

at each desired temperature and draw a graph through these values.

28.4.2.4.4 Calculate the specific heat,  $Cp_2$  (J/kg.°C), of the substance using:

$$Cp_2 = \frac{3600 \times (E_2 + K)}{C \times M_2} - \frac{H}{M_2}$$

where:

$E_2$	=	power applied to the internal heater (W)
C	=	slope of the curve on internal heating (sample) at the temperature of calculation (°C/h)
$M_2$	=	mass of sample (kg)



28.4.2.4.5 Calculate the heat generation,  $Q_T$  (W/kg), of the substance at intervals of 5 °C using the following formula for each temperature:

$$Q_T = \frac{(M_2 \times Cp_2 + H) \times \frac{D}{3600} - K}{M_2}$$

where:  $D$  = slope of the curve during the self-heating at the temperature of calculation (°C/h)

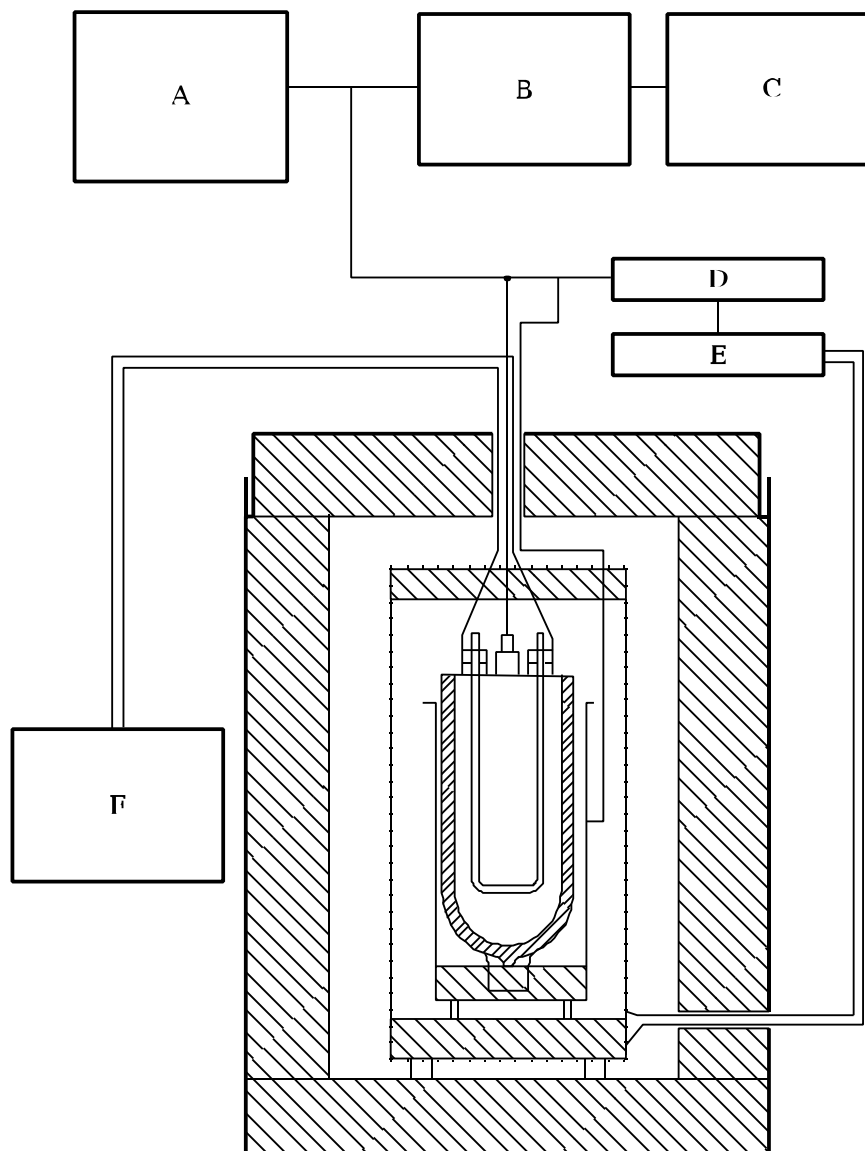
28.4.2.4.6 Plot the calculated rates of heat generation per unit of mass ( $Q_T$ ) as a function of the temperature in a graph with linear scales and draw the best-fit curve through the plotted points. Determine the heat losses per unit of mass,  $L$  (W/kg.°C) of the specific package, IBC or tank (see section 28.3.5). Draw a straight line of gradient  $L$  tangential to the heat generation curve. The intersection of the straight line and the abscissa is the critical ambient temperature, i.e. the highest temperature at which the substance as packaged does not show self-accelerating decomposition. The SADT is the critical ambient temperature (°C) rounded to the next higher multiple of 5 °C. An example is given in Figure 28.4.2.2.

28.4.2.5 *Examples of results<sup>a</sup>*

Substance	Mass (kg)	Packaging	Heat loss per unit mass (mW/kg.K)	SADT/SAPT (°C)
Azodicarbonamide	30	1G	100	> 75
tert-Butyl peroxybenzoate	25	6HG2	70	55
tert-Butyl peroxy-2-ethylhexanoate	25	6HG2	70	40
tert-Butyl peroxy-pivalate	25	6HG2	70	25
<b>N-Vinylformamide</b>	<b>1000</b>	<b>31H1</b>	<b>33</b>	<b>55</b>

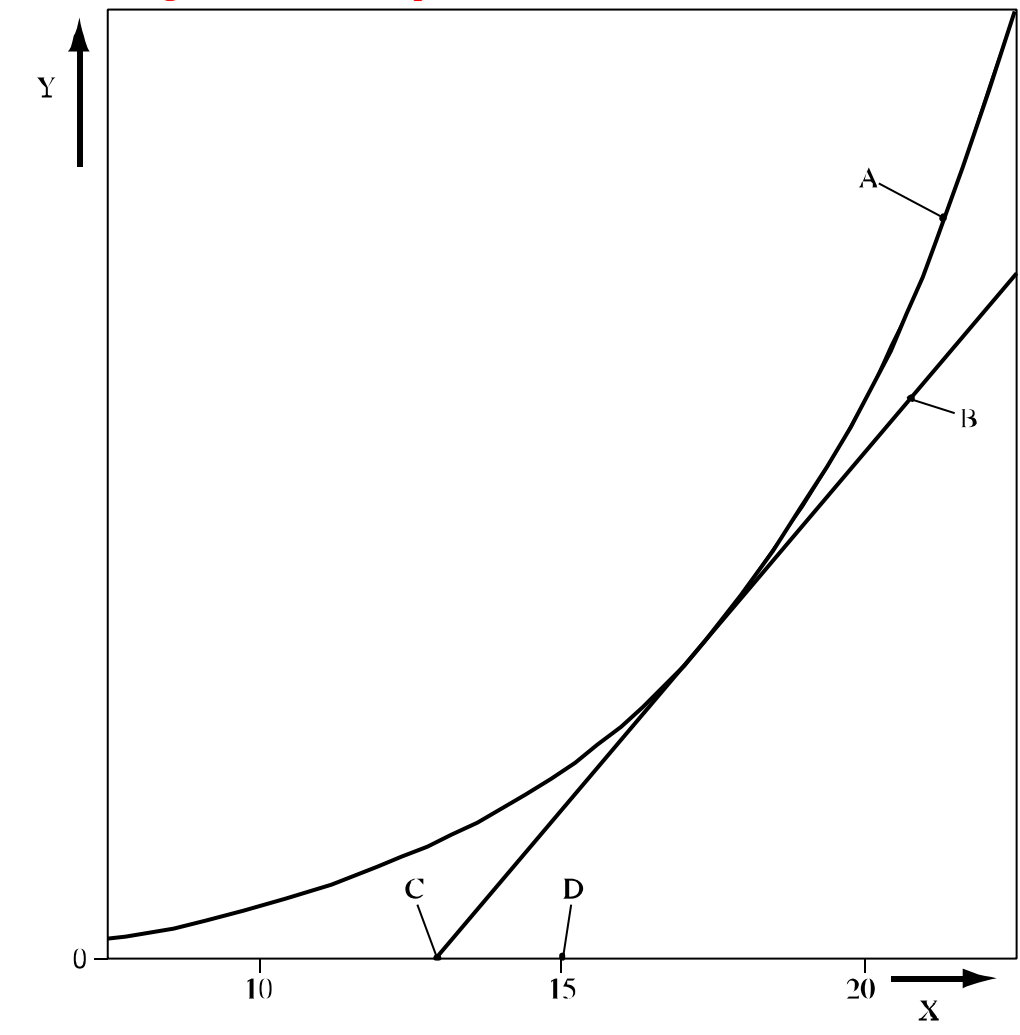
<sup>a</sup>These historical examples were determined using heat losses that are higher than those currently recommended for classification purposes (see table 28.4).

Figure 28.4.2.1: Adiabatic storage test



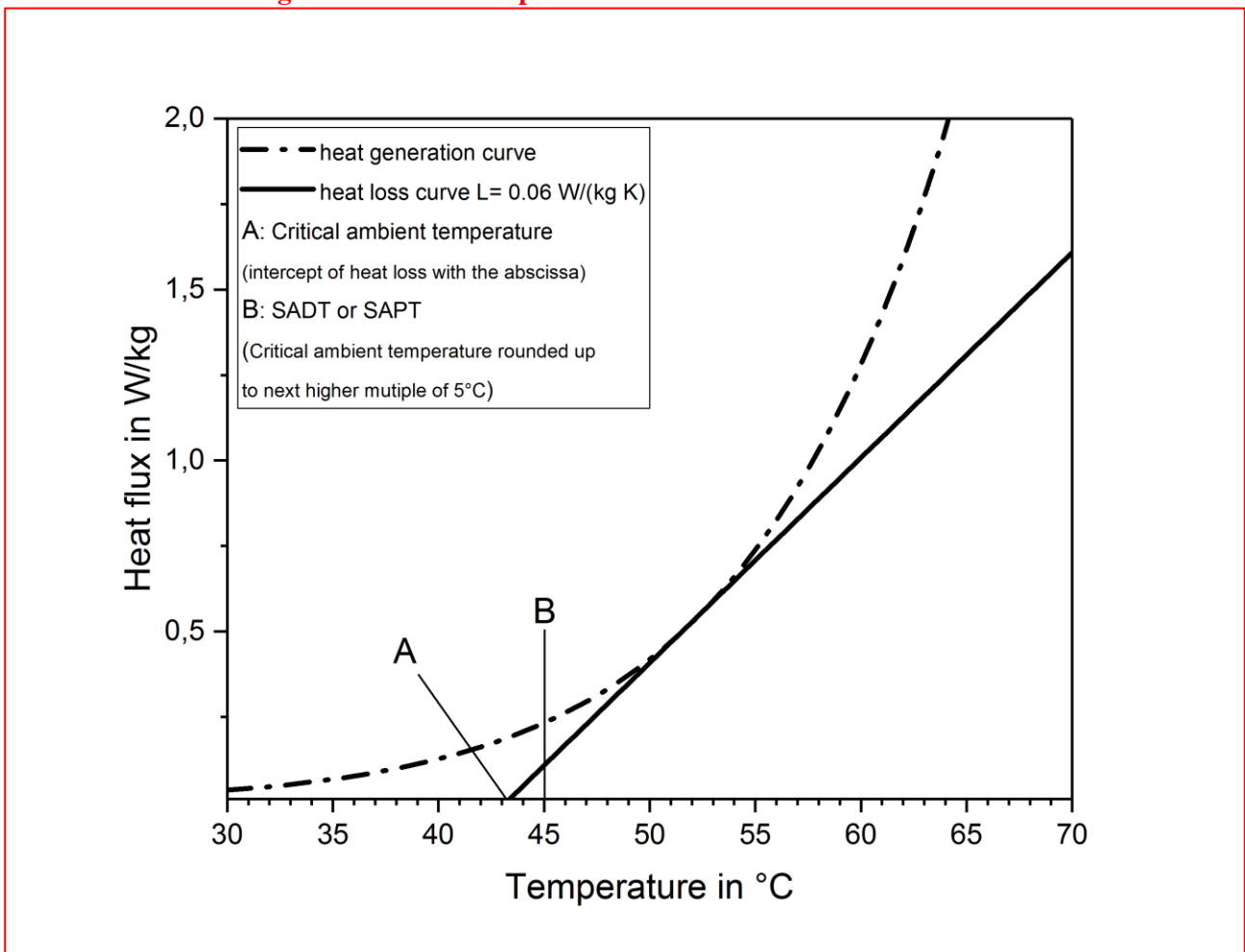
- 
- (A) Multi-point recorder and temperature controller (10 mV)
  - (B) External zero set
  - (C) Recorder set for greatest accuracy
  - (D) Control
  - (E) Relay
  - (F) Internal pre-heater
-

Figure 28.4.2.2: Example of determination of SADT or SAPT



- (A) Heat generation curve
- (B) Line with gradient equal to the rate of heat loss and tangential to the heat generation curve
- (C) Critical ambient temperature (intercept of heat loss line with the abscissa)
- (D) Self-accelerating decomposition temperature (SADT) — critical ambient temperature rounded up to next higher multiple of 5 °C
- (X) Temperature
- (Y) Heat flow (generation or loss) per unit mass

**Figure 28.4.2.2: Example of determination of SADT or SAPT**



### 28.4.3 *Test H.3: Isothermal storage test (IST)*

#### 28.4.3.1 *Introduction*

28.4.3.1.1 This method determines the rate of heat generation produced by reacting or decomposing substances as a function of time at constant temperature. The heat generation parameters obtained are used with the heat loss data relating to the package to determine the SADT or SAPT of a substance in its packaging. The method is appropriate for every type of packaging including IBCs and tanks. Some substances may show an increase in the rate of heat generation with increasing decomposition (e.g. due to autocatalysis or induced decomposition). This property is also taken into account by this test method.

~~28.4.3.1.2 Measurements can be performed in the temperature range of -20 °C to 200 °C. Heat generation values can be measured from 5 mW/kg to 5 W/kg. The thermal resistance between the sample holder and aluminium block via the heat flow meters is about 0.1 W/°C. The apparatus is able to measure rates of heat generation from 15 mW/kg to 1 500 mW/kg with a maximum error of 30% at 15 mW/kg and 5% from 100 to 1 500 mW/kg.~~

28.4.3.1.3.2 The ~~usually~~ robust construction of ~~the readily available~~ apparatus, the relatively small sample size and the well-defined operating conditions enable the test to be performed in an ordinary laboratory. The effects of a thermal explosion, e.g. fragmentation of the sample holder and generation of pressure, should be contained within the apparatus.

#### 28.4.3.2 *Apparatus and materials*

##### 28.4.3.2.1 *Isothermal Calorimetry (IC)*

~~Appropriate isothermal calorimeters can be used. The equipment should be able to measure heat generation values of 1 mW/kg to 1500 mW/kg in a temperature range of -20 °C to 200 °C. The maximum error in the heat generation should be less than 5 %. The equipment should be capable of maintaining the temperature to within 0.2 °C of the set temperature. Sample mass of test material should be at least 200 mg. Closed pressure resistant sample holders should be used and the material of the sample holder should not have catalytic effect on the decomposition behaviour of the test substance. This can be achieved by selecting the appropriate materials for the sample holders or by an appropriate passivation method of the sample holders.~~

~~28.4.3.2.1 The apparatus consists of an air-insulated heat sink (an aluminium block) which is kept at a constant temperature by means of controlled heating. A cryostat is used to maintain temperatures below 40 °C. The heat controller is capable of maintaining the temperature to within 0.2 °C of the set temperature. The temperature of the heat sink is measured with a platinum resistance sensor. The two holes drilled in the block contain heat flow meters (e.g. Peltier elements). A schematic drawing of the IST is given in Figure 28.4.3.1. For substances with an SADT or SAPT below ambient temperature, the test should be performed in a cooling chamber or solid carbon dioxide should be used for cooling the oven.~~

28.4.3.2.2 The sample ~~H~~holders ~~are~~ is placed on or around both heat flow meters. ~~one with the sample and one with an inert substance. Both holders are identical and have a volume of 70 cm<sup>3</sup>.~~ The amount of substance in ~~each~~ the sample holder is at least 200 mg ~~about 20 g~~. The material of the holders should be compatible with the sample. ~~are made of glass or stainless steel. The steel must be compatible with the test substance.~~ If an external reference is used it should be handled identical to the sample. ~~When using a glass holder, it is provided with a long capillary tube which prevents pressure build-up in the holder and evaporation of the sample.~~

28.4.3.2.3 The ~~voltage difference resulting from the difference in~~ heat flow from the sample holder to the heat sink and inert substance holder to the heat sink is continuously recorded as a function of time (differential measurement) by a recorder or computer.

#### 28.4.3.3 Procedure

##### 28.4.3.3.1 Calibration procedure

Before a measurement can be performed, the blank signal and the sensitivity of the heat flow meter need to be determined by the following applicable calibration procedure for the equipment used covering the temperature range of the measurement.

- ~~(a) Set the IST at the selected test temperature;~~
- ~~(b) Insert a heating coil in the sample holder. Fill the sample and reference holders with inert material (e.g. sodium chloride or milled glass beads) ensuring that the heating coil is completely covered with material. Place both holders in the IST;~~
- ~~(c) Determine the blank signal (the output of the recorder when no electric power is applied to the heating coil);~~
- ~~(d) Determine the sensitivity of the heat flow meter using two or three different electrical heating powers which lie within the expected range of heat generation of the sample to be tested.~~

##### 28.4.3.3.2 Test procedure

The test procedure is as follows:

- (a) Set the IST apparatus for the desired test temperature.; The temperature selected should be sufficient to give a rate of heat generation between 5 mW to 1000 mW per kg of substance or for tanks a maximum heat generation rate between 1 and 100 mW/kg;
- (b) Fill the sample holder with the weighed sample and with a representative quantity of packaging material (if metal) and insert the holder into the apparatus.; ~~The amount of sample should be sufficient to give a rate of heat generation between 5 mW to 1-500 mW per kg of substance;~~
- (c) Start monitoring the rate of heat production. ~~The results from the first 12 hours of the test should not be used because this period is required for temperature equilibration.~~ The duration of each test depends on the test temperature and on the rate of heat production. ~~The test should last for at least 24 hours after the 12 hour equilibration period but can then be stopped if the rate of heat generation is falling from the maximum or if the rate of heat generation is greater than 1.5 W/kg~~

The measuring time as given in Figure 28.4.3.1 can be used as guidance unless it leads to unrealistic measuring times (e.g. greater than 1000 hours). These measuring times are

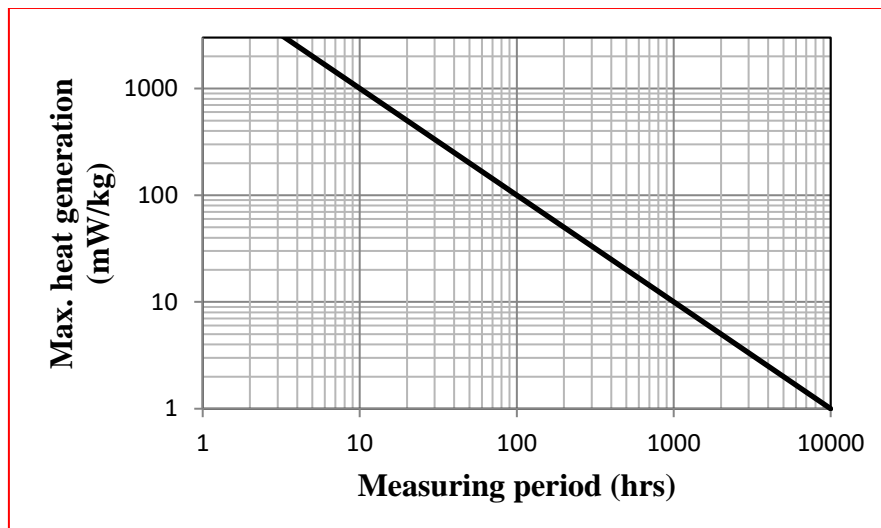
given to achieve a certain degree of conversion of the substance in order to take auto-catalytic effects into account;<sup>1,2</sup>

- (d) At the end of the test the change in sample mass should be determined;
- (e) The test is repeated with new samples at temperature intervals of 5 °C so that there are ~~at least five~~ ~~seven~~ results with a maximum heat generation rate between ~~15~~ and ~~15000~~ mW/kg ~~or for tanks a maximum heat generation rate between 1 – 100 mW/kg.~~

<sup>1</sup> J. L. C. van Geel, *Investigations into Self-Ignition Hazard of Nitrate Ester Propellants, Thesis, Technical University of Delft, The Netherlands, 1969.*

<sup>2</sup> Barendregt, R.B., *Thermal Investigation of Unstable Substances, Including a Comparison of Different Thermal Analytical Techniques, Thesis, Technical University of Delft, The Netherlands, 1981.*

Figure 28.4.3.1: Measuring period as a function of maximum heat generation measured



#### 28.4.3.4 Test criteria and method of assessing results

~~28.4.3.4.1~~ Calculate the sensitivity, S (mW/mV), of the instrument at the various electrical powers used in the calibration procedure using the following formula:

$$S = \frac{P}{U_d - U_b}$$

where: P = electric power (mW)  
~~U<sub>d</sub>~~ = dummy signal (mV)  
~~U<sub>b</sub>~~ = blank signal (mV)

~~28.4.3.4.2 Use these values and the test data to calculate the maximum rate of heat generation, Q (mW/kg), at the different test temperatures using the formula:~~

$$Q = \frac{(U_s - U_b) \times S}{M}$$

~~where:  $U_s$  = sample signal (mV)~~

~~$M$  = mass (kg)~~

28.4.3.4.13 Plot the calculated maximum rate of heat generation per unit of mass as a function of the test temperature on a graph with linear scales and draw the best-fit curve through the plotted points. Determine the heat losses per unit of mass, L (W/kg.°C) of the specific package, IBC or tank (see 28.3.5). Draw a straight line of gradient L tangential to the heat generation curve. The intersection of the straight line and the abscissa is the critical ambient temperature i.e. the highest temperature at which the substance as packaged does not show self-accelerating decomposition. The SADT or SAPT is the critical ambient temperature (°C) rounded to the next higher multiple of 5 °C. An example is given in Figure 28.4.3.2.

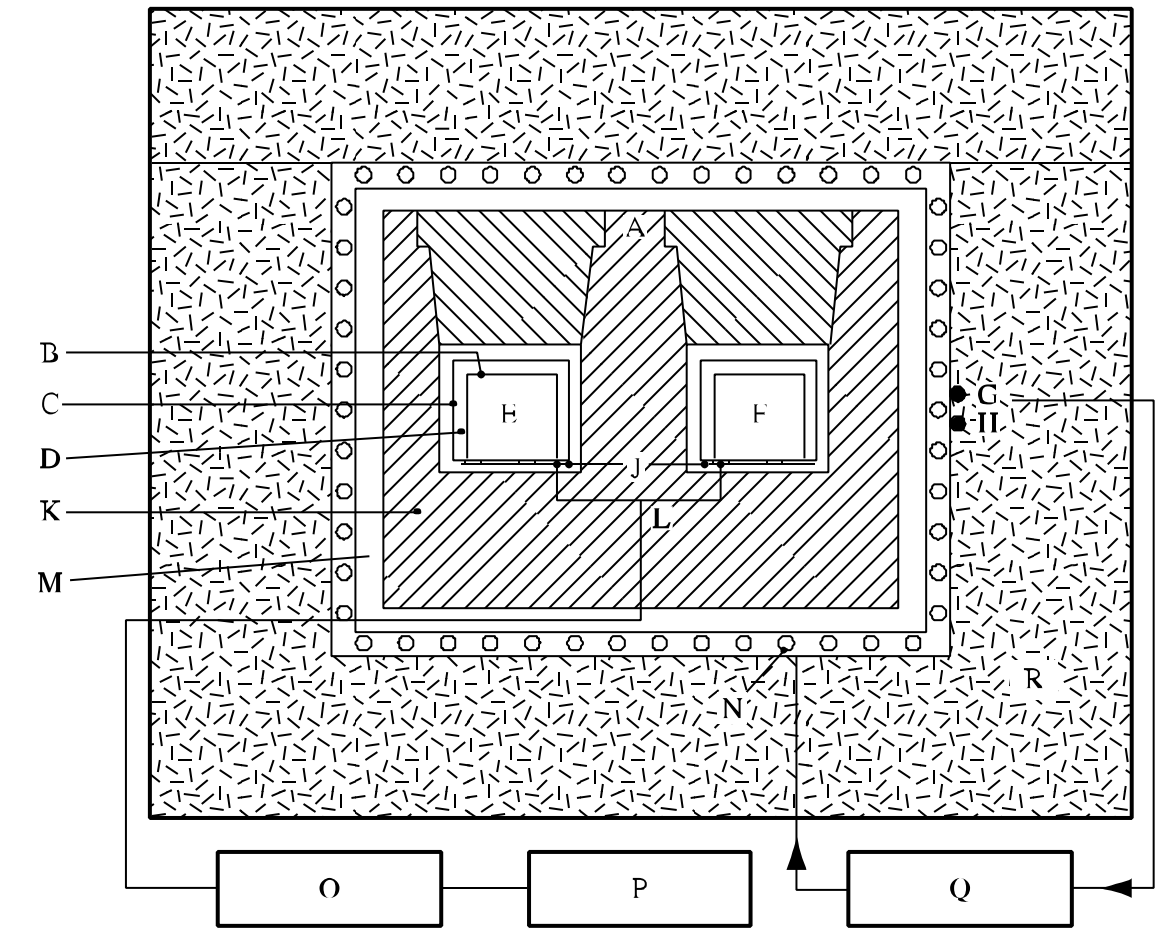
#### 28.4.3.5 Examples of results

Substance	Mass (kg)	Packaging	Heat loss per unit mass (mW/kg.K)	SADT/SAPT (°C)
Azodicarbonamide <sup>a</sup>	30	1G	100	> 75
tert-Butyl peroxybenzoate <sup>a</sup>	25	6HG2	70	55
tert-Butyl peroxy-2-ethylhexanoate <sup>a</sup>	25	6HG2	70	40
tert-Butyl peroxy-pivalate <sup>a</sup>	25	6HG2	70	25
2,5-Diethoxy-4-morpholinobenzenediazonium zinc chloride (90%) <sup>a</sup>	25	1G	150	45
2,5-Diethoxy-4-morpholinobenzenediazonium tetrafluoroborate (97%) <sup>a</sup>	25	1G	15	55
2,5-Diethoxy-4-(phenylsulphonyl)-benzenediazonium zinc chloride (67%) <sup>a</sup>	25	1G	15	50
2-(N-ethoxycarbonyl-N-phenylamino)-3-methoxy-4-(N-methyl-N-cyclohexylamino)-benzenediazonium zinc chloride (62%) <sup>a</sup>	25	1G	15	45
3-Methyl-4-(pyrrolidin-1-yl) benzenediazonium tetrafluoroborate (95%) <sup>a</sup>	25	1G	15	55
Cumyl peroxyneodecanoate (75%)	25	3H1	40	10
tert-Butyl peroxyneodecanoate	25	3H1	40	15
N-Vinylformamide	1000	31H1	33	55

<sup>a</sup>These historical examples were determined using heat losses that are higher than those currently recommended for classification purposes (see table 28.4).

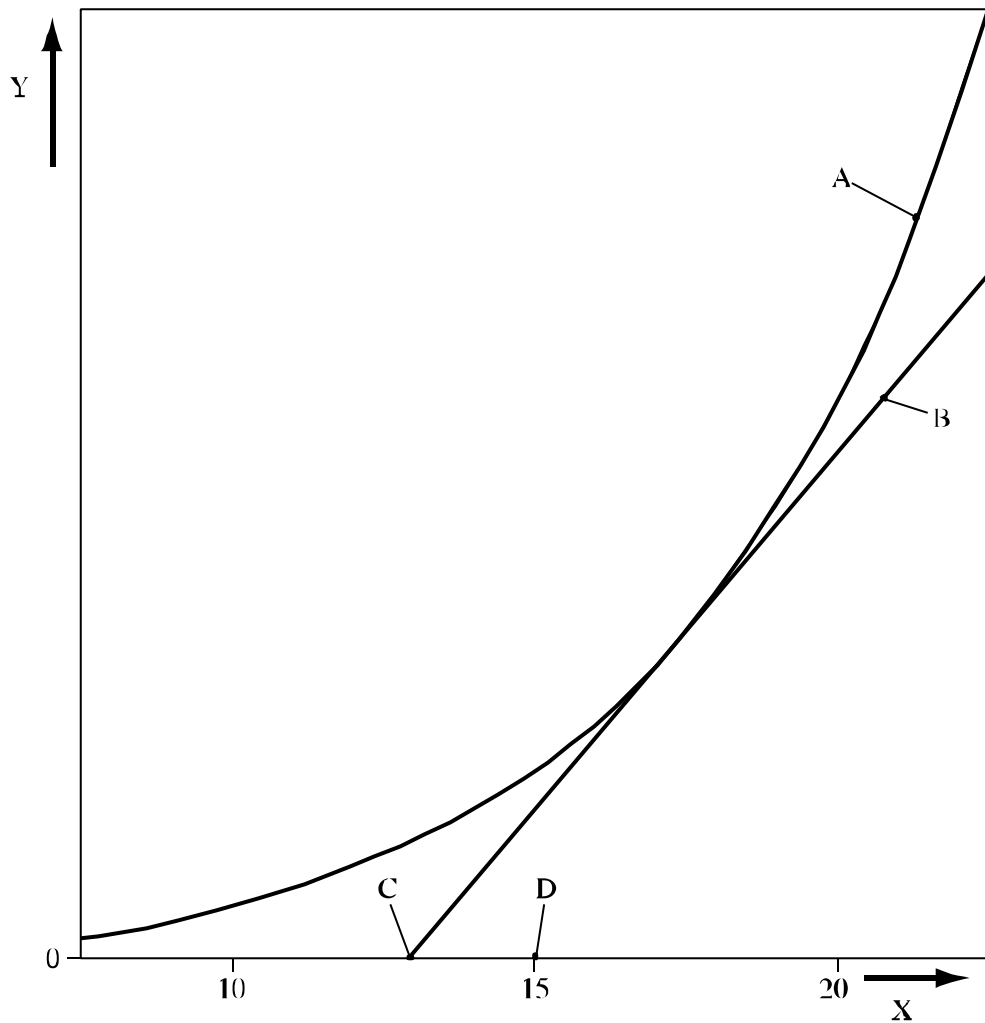


**Figure 28.4.3.1: Isothermal storage test**



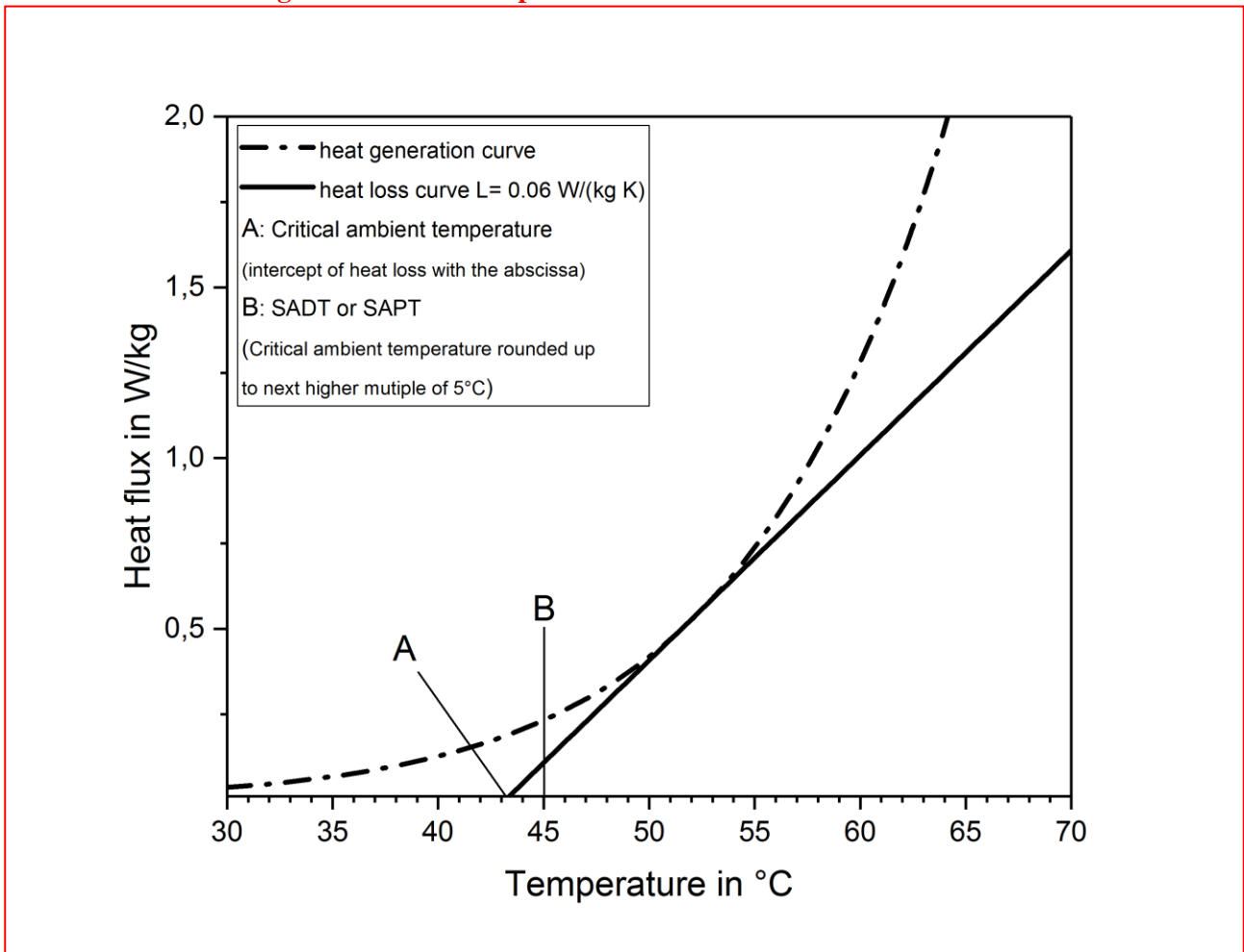
- |   |  |
|---|--|
| (A) — Platinum resistance thermometer                         | (B) — Sample vessel                                      |
| (C) — Cylindrical holder                                      | (D) — Air spaces   |
| (E) — Sample  | (F) — Inert material                                     |
| (G) — Platinum resistance sensor<br>— for temperature control | (H) — Platinum resistance sensor<br>— for safety control |
| (J) — Peltier elements  | (K) — Aluminium block                                    |
| (L) — Electric circuit  | (M) — Air space  |
| (N) — Heating wires   | (O) — Amplifier  |
| (P) — Recorder  | (Q) — Temperature controller                             |
| (R) — Glass wool  |  |

**Figure 28.4.3.2: Example of determination of SADT or SAPT**



- 
- (A) — Heat generation curve
  - (B) — Line with gradient equal to the rate of heat loss and tangential to the heat generation curve
  - (C) — Critical ambient temperature (intercept of heat loss line with the abscissa)
  - (D) — SADT or SAPT — critical ambient temperature rounded up to next higher multiple of 5 °C
  - (X) — Temperature
  - (Y) — Heat flow (generation or loss) per unit mass
-

**Figure 28.4.3.2: Example of determination of SADT or SAPT**



#### 28.4.4 *Test H.4: Heat accumulation storage test*

##### 28.4.4.1 *Introduction*

28.4.4.1.1 This method determines the minimum constant air environment temperature at which thermally unstable substances undergo exothermic decomposition or polymerization at conditions representative of the substance when packaged. The method is based on the Semenov theory of thermal explosion i.e. the main resistance to heat flow is considered to be at the vessel walls. The method can be used for the determination of the SADT or SAPT of a liquid substance in its packaging, including IBCs and small tanks (up to 2 m<sup>3</sup>) as well as for a solid substance in its packaging up to 50 kg.

28.4.4.1.2 The effectiveness of the method depends on selecting a Dewar vessel with heat loss per unit mass characteristics similar to the package offered for transport.

##### 28.4.4.2 *Apparatus and materials*

28.4.4.2.1 The experimental equipment consists of a suitable test chamber, appropriate Dewar vessels with closures, temperature probes and measuring equipment.

28.4.4.2.2 *The test should be performed in a test chamber—cell—capable of withstanding fire and overpressure and, preferably, should be fitted with a pressure relief system e.g. a blow out panel.* The recording system should be housed in a separate observation area.

28.4.4.2.3 For tests at temperatures up to 75 °C, a double walled metal chamber (ca. 250 mm inner diameter, 320 mm outer diameter and 480 mm high made from 1.5 mm to 2.0 mm thick stainless steel sheet) is can be used with fluid from a temperature-controlled circulating bath passed between the walls at the desired temperature. The test chamber is loosely closed by an insulated lid (e.g. made from 10 mm thick polyvinyl chloride). The air temperature in the double walled metal chamber should be controlled ~~should allow~~ so that the desired temperature for a liquid inert sample in the Dewar vessel to be maintained with a deviation of not more than ± 1 °C for up to 10 days. The air temperature in the double walled metal chamber and the sample temperature in the Dewar should be measured and recorded.

28.4.4.2.4 Alternatively, and particularly for tests at temperatures above 75 °C, a thermostatically controlled drying oven (which may be fan-assisted) large enough to allow air circulation on all sides of the Dewar vessel may be used. The air temperature in the oven should be controlled so that the desired temperature for a liquid inert sample in the Dewar vessel can be maintained with a deviation of not more than ± 1 °C for up to 10 days. The air temperature in the oven and the sample temperature in the Dewar should be measured and recorded. It is recommended that the door of the oven be fitted with a magnetic catch or replaced by a loosely fitting insulated cover. The oven may be protected by an appropriate steel liner and the Dewar vessel housed in a wire mesh cage.

28.4.4.2.5 For tests at sub-ambient temperatures, a double walled chamber (e.g. a freezer) of suitable size provided with a loose door or lid (e.g. with a magnetic closure) may be used. The temperature of the air in the chamber should be controlled to ± 1 °C of the set temperature. The air temperature in the chamber and the sample temperature in the Dewar should be measured and recorded.

28.4.4.2.6 Dewar vessels, with their closure system, are used with heat loss characteristics which are representative of the maximum ~~size-of~~ package size under investigation (see also table 28.4) ~~offered for transport~~. The closure of the Dewar vessel should be made of inert material. Particularly for solids, cork or rubber bungs may be used. An example of a closure system for use with liquids with low or medium volatility

**and wetted solids** is illustrated in Figure 28.4.4.1. Samples which are highly volatile at the test temperature should be tested in a pressure-tight ~~metal~~ vessel **that is made of a material compatible with the sample and** fitted with a pressure relief valve. The pressure vessel is placed in the Dewar vessel and the effect of the heat capacity of the metal vessel taken into account by calculation.

28.4.4.2.7 The heat loss characteristics of the system used, i.e. Dewar vessel and closure, should be established (see 28.3.6) prior to performance of the test. ~~Small adjustments to the heat loss characteristics of the Dewar can be achieved by varying the closure system. Since the closure system has a significant effect on the heat loss characteristics, these can be adjusted to some extent by varying the closure system.~~ In order to achieve the required level of sensitivity, Dewar vessels with sample capacities below 0.53 litres should not be used.

28.4.4.2.8 Dewar vessels **with a volume of 300 – 500 ml, filled at 80% with a liquid substance, with a heat loss of  $80 \text{ to } 100 \leq 40$  mW/kg.K** are normally suitable for representing a 225 l ~~50 kg~~ package **with a liquid substance**. For larger packages, IBCs or small tanks larger Dewar vessels with lower heat losses per unit mass should be used. ~~For example, spherical 1 litre Dewar vessels having heat loss characteristics in the range 16 to 34 mW/kg.K may be suitable for IBCs and small tanks.~~

#### 28.4.4.3 *Procedure*

28.4.4.3.1 Set the test chamber at the selected storage temperature. Fill the Dewar vessel, to 80% of its capacity, with the substance ~~to be tested under test~~ and note the mass of the sample. Solids should be moderately compressed. ~~In case of cylindrical Dewar vessel insert the temperature probe is inserted centrally 1/3 of the inner height of the Dewar from the bottom of the Dewar vessel. into the centre of the sample.~~ Seal the lid of the Dewar in place and insert the Dewar vessel in the test chamber, connect the temperature recording system and close the test chamber.

28.4.4.3.2 The sample is heated and the temperature of the sample and test chamber continuously monitored. The time is noted at which the sample temperature reaches a temperature 2 °C below the test chamber temperature. The test is then continued for a further seven days or until the sample temperature rises to 6 °C or more above the test chamber temperature ~~whichever if this occurs sooner. Note the time taken for the sample to rise from 2 °C below the test chamber temperature to its maximum temperature.~~

28.4.4.3.3 If the sample survives, cool and remove it from the test chamber and carefully dispose of it as soon as possible. The percentage mass loss and change in composition may be determined.

28.4.4.3.4 ~~Repeat the test with fresh samples, varying the storage temperature in 5 °C steps.~~ If the substance is being tested to determine if temperature control is necessary, perform sufficient tests, **in steps of 5 °C using fresh samples**, to determine the SADT or SAPT to the nearest 5 °C or to determine if the SADT or SAPT is ~~greater than or~~ equal to **or less than the applicable temperature specified in Table 28.2 60 °C**. If the substance is being tested to determine if it meets the SADT criterion for a self-reactive substance, perform sufficient tests to determine if the SADT for a 50 kg package is 75 °C or less. If the substance is being tested to determine if it meets the SAPT criterion for a polymerizing substance, perform sufficient tests to determine if the SAPT in the packaging as used is 75 °C or less.

#### 28.4.4.4 *Test criteria and method of assessing results*

28.4.4.4.1 The SADT or SAPT is reported as the lowest **chamber** temperature at which the sample ~~temperature undergoes~~ exceeds the ~~test~~ chamber temperature by 6 °C or more **within the seven days testing time frame (see paragraph 28.4.4.3.2)**. If the sample temperature does not exceed the ~~test~~ chamber temperature

by 6 °C or more in any test, the SADT or SAPT is recorded as being greater than the highest storage temperature used.

28.4.4.5 *Examples of results*

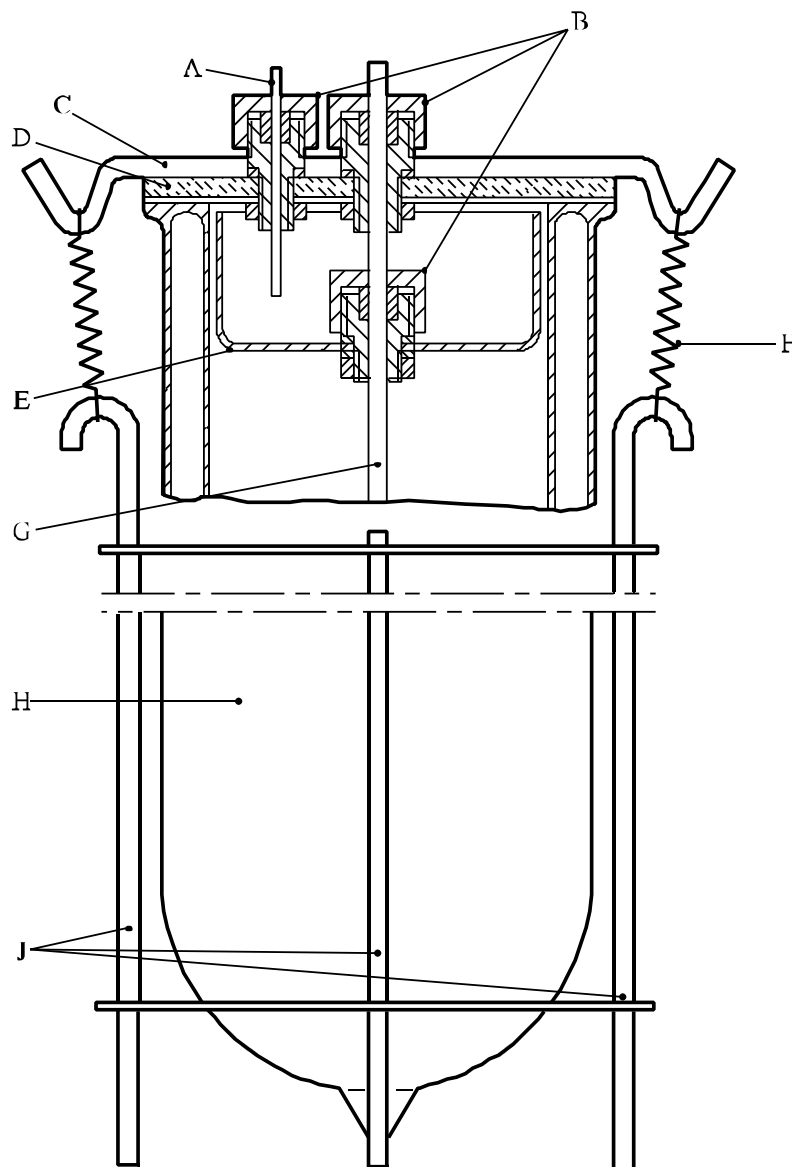
Substance	Sample mass (kg)	Dewar heat loss (mW/kg.K)	SADT/SAPT (°C)
Azodicarbonamide <sup>c</sup>	0.28	74	> 75
Azodicarbonamide, 90% with 10% activator <sup>c</sup>	0.21	70	55
2,2'-Azodi(isobutyronitrile)	<del>0.18</del> 0.28	<del>62</del> 27	50
Benzene-1,3-disulphohydrazide, 50% <sup>c</sup>	0.52	81	70
tert-Butyl hydroperoxide, 80% with 12% di-tert-butyl peroxide <sup>c</sup>	0.30	72	100 <sup>a</sup>
tert-Butyl peroxyneodecanoate, 40% <sup>c</sup>	0.42	65	25
tert-Butyl peroxy-3,5,5-trimethylhexanoate <sup>c</sup>	0.38	79	60
Dibenzoyl peroxide, 50% <sup>c</sup>	0.25	91	60
Di-(4-tert-butylcyclohexyl) peroxydicarbonate <sup>c</sup>	0.19	79	45
2,2-Di-(tert-butylperoxy)butane, 50% <sup>c</sup>	0.31	88	80
Di-(2-ethylhexyl) peroxydicarbonate <sup>c</sup>	0.39	64	0
2,5-Diethoxy-4-morpholinobenzenediazonium zinc chloride (66%) <sup>c</sup>	0.25	58	45
Diisotridecyl peroxydicarbonate <sup>c</sup>	0.38	80	10
Peroxyacetic acid, 15%, with 14% hydrogen peroxide (type F) <sup>c</sup>	1.00	33	> 50 <sup>b</sup>
Dilauroyl peroxide, technically pure	0.16	26	50
Didecanoyl peroxide technically pure	0.20	28	40
N-Vinylformamide	0.40	33	55

<sup>a</sup> In a pressure vessel contained with a 2 litres Dewar vessel.

<sup>b</sup> In a spherical, 1 litre Dewar vessel.

<sup>c</sup> These historical examples were determined using heat losses that are higher than those currently recommended for classification purposes (see table 28.4).

Figure 28.4.4.1: Dewar vessel with closure for testing liquids and wetted solids



- |                            |  |
|----------------------------|--|
| (A) PTFE capillary tube    | (B) Special screw fittings (PTFE or Al) with O-ring seal |
| (C) Metal strip            | (D) Glass lid  |
| (E) Glass beaker base      | (F) Spring   |
| (G) Glass protective tube  | (H) Dewar vessel   |
| (J) Steel retaining device |  |

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