

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

6 December 2010

**Sub-Committee of Experts on the
Transport of Dangerous Goods**

Thirty-eighth session

Geneva, 29 November–7 December 2010

Item 11 of the provisional agenda

**Issues relating to the Globally Harmonized
System of Classification and Labelling of
Chemicals (GHS)**

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

Twentieth session

Geneva, 7–9 December 2010

Item 2(a) of the provisional agenda

**Updating of the third revised edition of the Globally
Harmonized System of Classification and Labelling of
Chemicals (GHS): Physical hazards**

**Clarifications to the proposal in ST/SG/AC.10/C.3/2010/69 –
ST/SG/AC.10/C.4/2010/9**

Transmitted by the expert from the United States of America

1. This paper proposes clarifications to the Annex contained in document ST/SG/AC.10/C.3/2010/69- ST/SG/AC.10/C.4/2010/9 and corresponding changes to the test method proposed in ST/SG/AC.10/C.3/2010/70- ST/SG/AC.10/C.4/2010/10.

2. Changes to proposed GHS amendments associated with ST/SG/AC.10/C.3/2010/69- ST/SG/AC.10/C.4/2010/9 are provided in Annex 1. The proposed clarifications, in bold and italicized print, are as follows:

(a) Section 2.2.2.2:

- Rename the proposed additional categories 1 and 2 to “a” and “b,” respectively. This change is proposed to avoid the potential misinterpretation that additional category 1 would only modify Category 1 flammable gas and similarly that additional category 2 would only modify category 2 flammable gas.
- Include the specific temperature (20°C) and pressure (101.3 kPa) in the criteria in Table 2.2.2.

(b) Section 2.2.3: The proposed additional categories are renamed and the word “additional” is added prior to the words symbol and signal word for additional categories a and b. The use of the word “additional” in this table is to ensure that that a category 1 flammable gas would retain the flame pictogram if it is also classified as an unstable gas.

- Section logic 2.2(b): The proposed decision logic is modified to reflect the changes identified above.

3. Changes to the proposed test method associated with ST/SG/AC.10/C.3/2010/70- ST/SG/AC.10/C.4/2010/10 are provided in Annex 2. The proposed changes, in bold and italicized print, correspond to those made in paragraph 2 above, and are as follows:

(a) Table 3x.1: In the Classification column, the classifications identified have been updated to reflect the new categories “a” and “b,” respectively.

(b) Section 3x.4.5.1: The category criteria is corrected to reflect the proposed changes for the new categories “a” and “b,” respectively.

Annex 1

Proposed amendments to the GHS

Chapter 2.2

Flammable gases (including chemically unstable gases)

2.2.1 Definitions

2.2.1.1 A flammable gas is a gas having a flammable range with air at 20 °C and a standard pressure of 101.3 kPa.

2.2.1.2 A chemically unstable gas is a flammable gas that is able to react explosively even in the absence of air or oxygen

2.2.2 Classification criteria

2.2.2.1 A flammable gas is classified in one of the two categories for this class according to the following table:

Table 2.2.1: Criteria for flammable gases

Category	Criteria
1	Gases, which at 20 °C and a standard pressure of 101.3 kPa: (a) are ignitable when in a mixture of 13% or less by volume in air; or (b) have a flammable range with air of at least 12 percentage points regardless of the lower flammable limit.
2	Gases, other than those of Category 1, which, at 20 °C and a standard pressure of 101.3 kPa, have a flammable range while mixed in air.

NOTE 1: Ammonia and methyl bromide may be regarded as special cases for some regulatory purposes.

NOTE 2: Aerosols should not be classified as flammable gases. See Chapter 2.3.

2.2.2.2 A flammable gas that is also chemically unstable is additionally classified in one of the two categories for chemically unstable gases [using the methods described in Part III of the Manual of Tests and Criteria] according to the following table:

Table 2.2.2: Criteria for chemically unstable gases

<u>Additional category of chemically unstable gas</u>	<u>Criteria</u>
<u>a</u>	<u>Flammable gases which are chemically unstable at 20 °C and a standard pressure of 101.3 kPa.</u>
<u>b</u>	<u>Flammable gases which are chemically unstable at a temperature greater than 20 °C and/or a pressure greater than 101.3 kPa.</u>

2.2.3 Hazard communication

General and specific considerations concerning labelling requirements are provided in *Hazard communication: Labelling* (Chapter 1.4). Annex 2 contains summary tables about classification and labelling. Annex 3 contains examples of precautionary statements and pictograms which can be used where allowed by the competent authority.

Table 2.2.3: Label elements for flammable gases (including chemically unstable gases)

	Flammable gas		Chemically unstable gas	
	Category 1	Category 2	Additional category a	Additional category b
Symbol	Flame	<i>No symbol</i>	<i>No additional symbol</i>	<i>No additional symbol</i>
Signal word	Danger	Warning	<i>No additional signal word</i>	<i>No additional signal word</i>
Hazard statement	Extremely flammable gas	Flammable gas	<u>May react explosively even in the absence of air</u>	<u>May react explosively even in the absence of air at elevated pressure and/or temperature</u>

2.2.4 Decision logic and guidance

The decision logic and guidance, which follow, are not part of the harmonized classification system, but have been provided here as additional guidance. It is strongly recommended that the person responsible for classification studies the criteria before and during use of the decision logic.

2.2.4.1 Decision logic for the classification of flammable gases

To classify a flammable gas, data on its flammability are required. The classification is according to decision logic 2.2 (a).

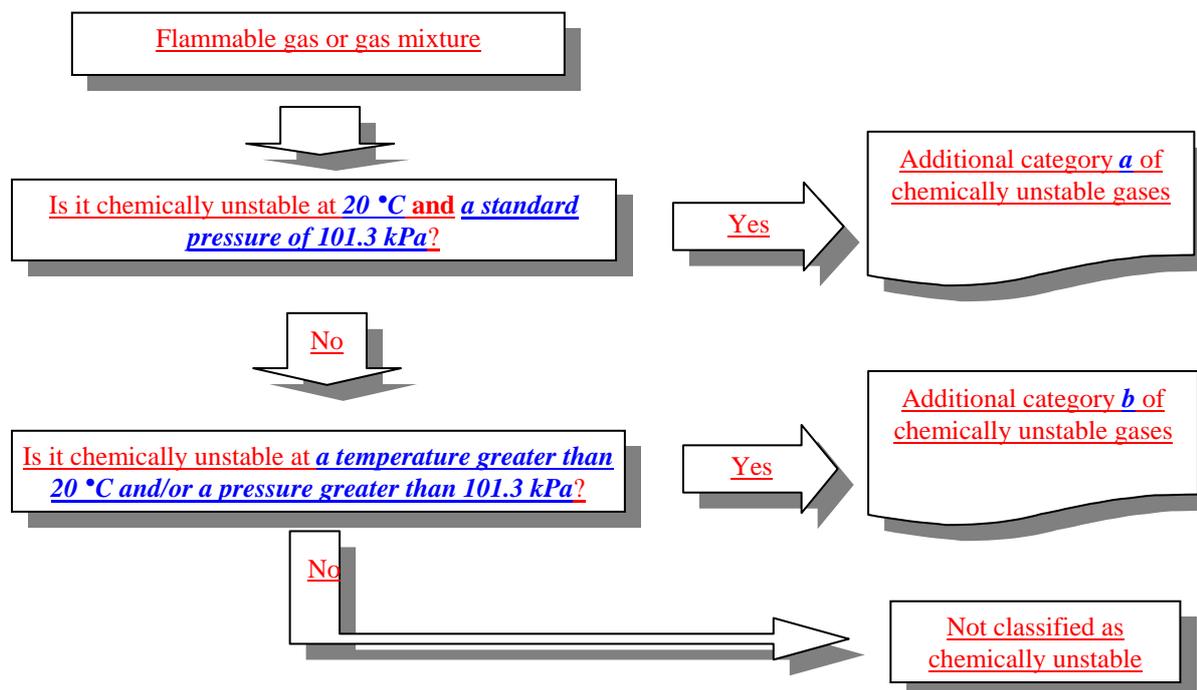
Decision logic 2.2 (a)

<Unchanged decision logic as currently in section 2.2.4.1>

2.2.4.2 Decision logic for the classification of chemically unstable gases

To classify a flammable gas as chemically unstable, data on its chemical instability are required. The classification is according to decision logic 2.2 (b).

Decision logic 2.2 (b)



2.2.4.3 *Guidance*

Flammability should be determined by tests or by calculation in accordance with methods adopted by ISO (see ISO 10156:2010 “Gases and gas mixtures – Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets”). Where insufficient data are available to use these methods, tests by a comparable method recognized by the competent authority may be used.

Chemical instability should be determined in accordance with the method described in [ST/SG/AC.10/C.4/2010/10 (www.unece.org/trans/main/dgdb/dgsubc4/c42010.html)] [Part III of the Manual of Tests and Criteria]. If the calculations in accordance with ISO 10156:2010 show that a gas mixture is not flammable it is not necessary to carry out the tests for determining chemical instability for classification purposes.

2.2.5 **Example: Classification of a flammable gas mixture by calculation according to ISO 10156:2010**

<Unchanged text as currently in section 2.2.5>

Annex 2

Proposed amendments to the Manual of Tests and Criteria

Insert the following new section in Part III:

SECTION [3x]

DETERMINATION OF CHEMICAL INSTABILITY OF GASES AND GAS MIXTURES

3x.0 Introduction

This section presents the United Nations scheme for the classification of gases and gas mixtures as chemically unstable. The text should be used in conjunction with the classification principles given in Chapter 2.2 of the GHS and the test methods given in this section.

3x.1 Purpose

3x.1.1 This test method is used to determine the chemical instability of a gas or gas mixture by ignition tests in a closed vessel at ambient and elevated temperature and pressure.

3x.1.2 For the purposes of this test method the following definitions apply:

Chemical instability, propensity of a gas or gas mixture to react dangerously even in the absence of any reaction partner (e.g. air or oxygen) by decomposing and thereby causing a temperature and/or pressure increase;

Test gas, gas or gas mixture to be evaluated by this test method;

Corresponding initial pressure, pressure at which the test at 65 °C is carried out. For test gases that are completely gaseous the corresponding initial pressure is the pressure that a gas develops at 65 °C based on the maximum (filling) pressure at ambient temperature. For liquefied test gases the corresponding initial pressure is the vapour pressure at 65 °C.

3x.2 Scope

3x.2.1 The test method does not cover gas decomposition under process conditions in chemical plants and possible dangerous reactions between different gases in gas mixtures.

3x.2.2 Mixtures of gases, where the components can react dangerously with each other, e.g. flammable and oxidizing gases, are not regarded as chemically unstable in the sense of this test method.

3x.2.3 If the calculations in accordance with ISO 10156:2010 show that a gas mixture is not flammable it is not necessary to carry out the tests for determining chemical instability for classification purposes.

3x.2.4 Expert judgement should be applied to decide whether a flammable gas or gas mixture is a candidate for classification as chemically unstable in order to avoid unnecessary testing of gases where there is no doubt that they are stable. Functional groups indicating chemical instability in gases are triple-bonds, adjacent or conjugated double-bonds, halogenated double-bonds and strained rings.

3x.3 Concentration limits

3x.3.1 Generic concentration limit

3x.3.1.1 Gas mixtures containing only one chemically unstable gas are considered as chemically stable and therefore do not have to be tested for classification purposes if the concentration of the chemically unstable gas is below the higher of the following generic concentration limit:

- (a) The lower explosion limit (LEL) of the chemically unstable gas; or
- (b) 3 mole%.

3x.3.2 Specific concentration limits

3x.3.2.1 The following tables contain information about some gases with regard to their classification as chemically unstable. Specific concentration limits for their mixtures are given. Gas mixtures containing only one chemically unstable gas in concentrations below the specific concentration limit are considered as chemically stable and therefore do not have to be tested for classification purposes.

Table 3x.1: Information about gases with regard to their chemical instability and concentration limits for their mixtures below which the mixtures are not classified as chemically unstable

Information about the pure gas					Information about its mixtures
Chemical Name	Molecular formula	CAS No	UN No	Classification	Specific concentration limit (see Notes 1 and 2)
Acetylene	C ₂ H ₂	74-86-2	1001 3374	Chem. Unst. Cat. a	See Table 3x.2 For other mixtures: Partial pressure of 1 bar abs
Bromotrifluoro-ethylene	C ₂ BrF ₃	598-73-2	2419	Chem. Unst. Cat. b	8.4 mole% (LEL)
Butadiene-1,2	C ₄ H ₆	590-19-2	1010	Not classified as chemically unstable	
Butadiene-1,3	C ₄ H ₆	106-99-0	1010	Not classified as chemically unstable	
Butyne-1, Ethylacetylene	C ₄ H ₆	107-00-6	2452	Chem. Unst. Cat. b	The specific concentration limits for acetylene may be applied, see Table 3x.2. For other mixtures: Partial pressure of 1 bar abs
Chlorotrifluoro-ethylene	C ₂ ClF ₃	79-38-9	1082	Chem. Unst. Cat. b	4.6 mole% (LEL)
Ethylene oxide	C ₂ H ₄ O	75-21-8	1040	Chem. Unst. Cat. a	30 mole % for mixtures with nitrogen or carbon dioxide For other mixtures: [values to be added before end December 2010]
Vinyl methyl ether	C ₃ H ₆ O	107-25-5	1087	Chem. Unst. Cat. b	3 mole%
Propadiene	C ₃ H ₄	463-49-0	2200	Chem. Unst. Cat. b	The specific concentration limits for acetylene may be applied, see Table 3x.2. For other mixtures: Partial pressure of 1 bar abs

Information about the pure gas					Information about its mixtures
Chemical Name	Molecular formula	CAS No	UN No	Classification	Specific concentration limit (see Notes 1 and 2)
Propyne	C ₃ H ₄	74-99-7	3161	Chem. Unst. Cat. <u>b</u>	The specific concentration limits for acetylene may be applied, see Table 3x.2. For other mixtures: Partial pressure of 1 bar abs
Tetrafluoroethylene	C ₂ F ₄	116-14-3	1081	Chem. Unst. Cat. <u>b</u>	10.5 mole% (LEL)
Trifluoroethylene	C ₂ HF ₃	359-11-5	1954	Chem. Unst. Cat. <u>b</u>	10.5 mole % (LEL)
Vinyl bromide	C ₂ H ₃ Br	593-60-2	1085	Chem. Unst. Cat. <u>b</u>	5.6 mole% (LEL)
Vinyl chloride	C ₂ H ₃ Cl	75-01-4	1086	Chem. Unst. Cat. <u>b</u>	3.8 mole% (LEL)
Vinyl fluoride	C ₂ H ₃ F	75-02-5	1860	Chem. Unst. Cat. <u>b</u>	3 mole%

Note 1: The maximum pressure should be limited in order to avoid condensation.

Note 2: The test method is not applicable to liquefied gas mixtures. In case the gaseous phase above a liquefied gas mixture may become chemically unstable after withdrawal, this shall be communicated via the safety data sheet.

Table 3x.2: Specific concentration limits for binary mixtures with acetylene. These concentration limits may also be applied to butyne-1 (ethylacetylene), propadiene and propyne

Concentration limit for acetylene in mol %	Maximum (filling) pressure in bar for a mixture with						
	N ₂	CO ₂	NH ₃	H ₂	CH ₄	C ₃ H ₈	C ₂ H ₄
3.0	200.0						
4.0	100.0						
5.0				40.0			40.0
6.0	80.0						
8.0	60.0						
10.0	50.0	38.0	5.6	20.0	100.0	6.0	20.0
15.0	30.0	30.0		10.0			10.0
20.0	25.0	20.0	6.2	5.0	50.0	6.6	7.5
25.0	20.0	15.0					5.0
30.0	10.0	10.0	6.9		25.0	7.3	
35.0			7.3				
40.0					15.0	8.2	
45.0							
50.0					5.0	9.3	
60.0						10.8	

3x.4 Test method

3x.4.1 Introduction

3x.4.1.1 The propensity of a gas to decompose depends strongly on pressure, temperature and in case of gas mixtures on the concentration of the chemically unstable component. The possibility of decomposition reactions shall be evaluated at conditions which are relevant for handling and use and transport. Therefore two types of tests shall be performed:

- a) At ambient temperature and pressure,
- b) At 65 °C and the corresponding initial pressure

3x.4.2 Apparatus and material

3x.4.2.1 The test apparatus (see Figure 3x.1) consist of a pressure resistant test vessel (heatable) made of stainless steel; an ignition source; a measuring and recording system to record the pressure inside the ignition vessel; a gas supply; a venting system with bursting disk and additional piping, fitted with remote-controlled valves and cocks.

- (a) Pressure resistant test vessel

The test vessel is a cylindrical stainless steel vessel with an inner volume of about 1 dm³ and an inner diameter of 80 mm. An exploding wire ignition source is screwed into the bottom of the vessel. The vessel is equipped with a heating jacket which is connected to a temperature control unit that heats the outer vessel wall with an accuracy of ± 2 K. The test vessel is insulated with temperature resistant insulation material to avoid heat loss and temperature gradients. The test vessel shall be pressure resistant up to 500 bar (50 MPa).

- (b) Exploding wire igniter

The ignition source is an exploding (fusing) wire igniter similar to that described in ASTM E 918 and EN 1839. The igniter consists of two insulated electrodes at 3 mm to 6 mm distance, holding a nickeline wire of 0.12 mm diameter at its ends. The ignition energy is provided by a 1.5 kVA/230 (115) V insulating transformer, which is switched for a short time period to this igniter. The wire melts and then an electrical arc burns between the electrodes for a period extending in maximum to half a period of the supply voltage (10 (8.3) ms). An electronic control unit allows switching different time periods of the mains voltage half wave to the igniter. The corresponding energy delivered shall be in the range of 15 J ± 3 J. The energy can be measured by recording the current and voltage during ignition.

- (c) Pressure and temperature recording equipment

The pressure inside the ignition vessel shall be measured with a calibrated piezoresistive pressure transducer. The measuring range shall be 20 times higher than the initial pressure. The sensitivity shall be at least 0.1 % of the full scale and the accuracy shall be better than 0.5 % of the full scale.

The temperature of the ignition vessel shall be measured and controlled with a 3 mm thermocouple type “K” (NiCr/NiAl) mounted 50 mm below the top inside the autoclave.

After ignition the digitized pressure signal shall be recorded with a computer. The initial pressure (p_0) and the highest pressure (p_{ex}) are derived from the raw data.

(d) Gas supply

Two different types of gas supply are necessary, one for test gases that are completely in the gaseous phase and one for liquefied test gases. Test gases in the gaseous phase are metered volumetric or by flow measurement and liquefied test gases are metered gravimetric.

(e) Bursting disk

The bursting disk is supposed to protect the test vessel. It is connected to a vent pipe for the exhaust gas. The free diameter of the bursting disk should be at least 10 mm, the inner diameter of the pipe at least 15 mm. The opening pressure of the bursting disk shall amount to 250 bar (25 MPa).

(f) Additional piping and valves

The piping and valves which are fitted directly to the test vessel, shall be pressure resistant up to 500 bar (50 MPa). The test apparatus shall be operated by remotely operated valves.

3x.4.3 Test procedure

3x.4.3.1 The test gas is charged into a pressure resistant stainless steel vessel at controlled temperature and pressure. The vessel is equipped with a bursting disk. Ignition of the test gas is achieved with an exploding wire igniter. Whether a decomposition reaction has occurred is deduced from the pressure rise produced.

3x.4.3.2 The tests shall be executed in the following sequence:

(a) Test at ambient temperature and pressure

For the tests at 25 °C and 1.01 bar (101.3 kPa) the exploding wire igniter shall be arranged in the middle of the test vessel. The test vessel and the piping are evacuated. The test gas is filled into the test vessel by using the remotely operated valves until ambient pressure (initial pressure) is reached. After closing the valves the igniter is fired. The ignition energy shall be about 15 J to avoid over-initiation in the test vessel at this relatively low pressure. Criterion for a reaction is a pressure rise of more than 20 % after ignition ($f = p_{ex}/p_0 > 1.20$). If no such pressure rise has occurred two further re-tests shall be carried out.

If the test gas shows a pressure rise of more than 20 % in either of the tests it is to be classified as "chemically unstable at ambient temperature and pressure". No further tests are required.

(b) Test at elevated temperature and pressure

If in the tests according to 3x.4.3.2 (a) no pressure rise of more than 20 % has occurred, further tests at 65 °C and the corresponding initial pressure shall be performed. The procedure is the same as in 3x.3.3.2 (a) but care should be taken with potentially unstable gases under pressure. The ignition energy shall be about 15 J. If no pressure rise of more than 20 % has occurred two further re-tests shall be carried out.

If the test gas shows a pressure rise of more than 20 % in either of the tests it is to be classified as “chemically unstable at elevated temperature and/or pressure”.

3x.4.4 Safety precautions

3x.4.4.1 Adequate shielding of the test apparatus must be provided to prevent injury in the event of equipment rupture. The apparatus is to be set up in such a way that the operator does not have to be in the same room as long as the vessel contains test gas. Alternatively, the test apparatus is separated by a blast proof barrier from the operator. Activation of the ignition source should be possible only from a position shielded from the test vessel.

3x.4.4.2 The test vessel shall be fitted with a bursting disk connected to a vent pipe that allows venting the exhaust gas safely. Therefore it has to be taken into account that the exhaust gas can be hazardous itself (e.g. flammable or toxic).

3x.4.4.3 The gas cylinder containing the test gas shall be equipped with a non-return valve and shall be separated from the test apparatus before the igniter is fired to avoid backfiring into the cylinder. The cylinder valve has to be closed immediately after finishing the filling.

3x.4.4.4 Some chemically unstable gases can explode very violently especially at higher pressures. Therefore it is strongly recommended to start with the experiments at atmospheric pressure.”

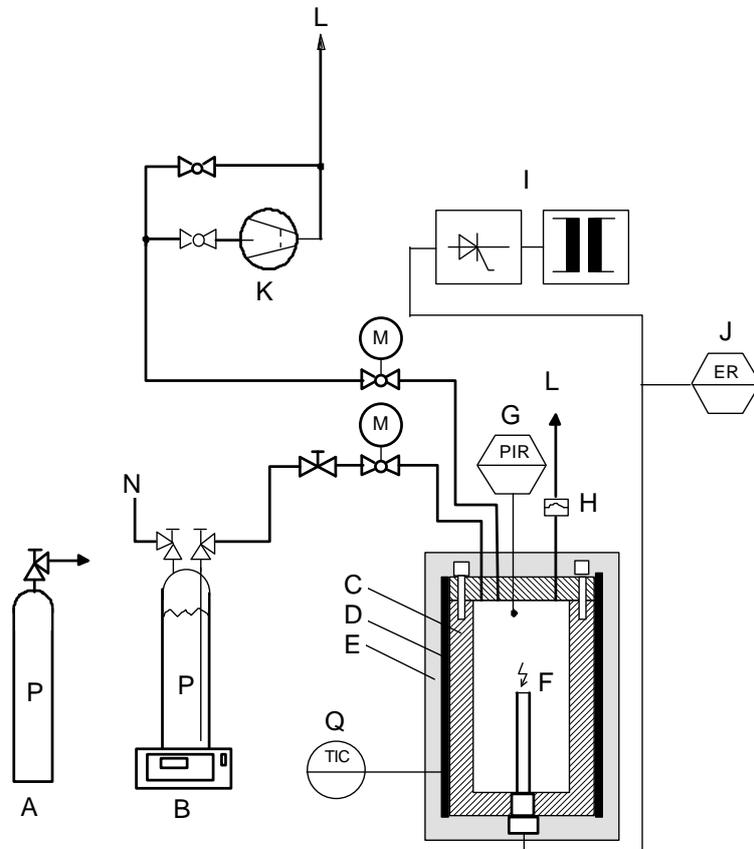
3x.4.5 Test criteria and method of assessing results

3x.4.5.1 Chemically unstable gases or gas mixtures shall be classified as “chemically unstable at 20 °C and a standard pressure of 101.3 kPa” or “chemically unstable at a temperature greater than 20 °C and/or a pressure greater than 101.3 kPa” according to the test results as follows:

- (a) The gas is classified as “chemically unstable at 20 °C and a standard pressure of 101.3 kPa” if the test at 25 °C and 1.01 bar (101.3 kPa) shows a pressure rise of more than 20 % of the initial absolute pressure.
- (b) The gas is classified as “chemically unstable at a temperature greater than 20 °C and/or a pressure greater than 101.3 kPa” if the test at 65 °C and the corresponding initial pressure shows a pressure rise of more than 20 % of the initial absolute pressure but no such pressure rise at 25 °C and 1.01 bar (101.3 kPa).

3x.4.5.2 The gas is not classified according to this test method (i.e: it is chemically stable) if it does not show a pressure rise of more than 20 % of the initial absolute pressure in either of the tests.

NOTE: *Chemically unstable gases not submitted to the classification procedure in this section should be classified as chemically unstable, category 1 (see Chapter 2.2 of the GHS).*



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| (A) Test gas supply (gaseous) | (B) Test gas supply (liquefied) |
| (C) Pressure resistant test vessel | (D) Regulated electric heater |
| (E) Thermal insulation | (F) Exploding wire igniter |
| (G) Pressure sensor, pressure indication and registration (PIR) | (H) Bursting disk |
| (I) Electronic ignition device | (J) Energy registration (ER) |
| (K) Vacuum pump | (L) Exhaust gas |
| (M) Motor controlled valve | (N) Pressurized helium |
| (P) Test gas | (Q) Temperature sensor, temperature indication and control (TIC) |

Figure 3x.1: Test apparatus