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Gas cylinders — Gases and gas mixtures — Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets

Bouteilles à gaz — Gaz et mélanges de gaz — Détermination du potentiel d'inflammabilité et d'oxydation pour le choix des raccords de sortie de robinets

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 58, *Gas cylinders*, Subcommittee SC 2, *Cylinder fittings*.

This fourth edition cancels and replaces the third edition (ISO 10156:2010), which has been technically revised. It also incorporates ISO 10156:2010/Cor 1:2010.

The main changes compared to the previous edition are as follows:

— 4.1, 4.2.5 and 4.4 have been technically revised;

— 4.5 and 4.6 have been added.

Introduction

ISO 5145 specifies the dimensions of different cylinder valve outlets for different compatible gas groups. These compatible gas groups are determined according to practical criteria defined in ISO 14456.

These criteria are based on certain physical, chemical, toxic and corrosive properties of the gases. In particular, the flammability in air and the oxidizing ability are considered in this document.

One of the potential complications that prompted the development of this document is that while there are abundant data in the literature relating to pure gases, differences can be found, depending upon the test methods employed. In the case of gas mixtures, data in the literature are often incomplete or even non-existent.

The initial aim of this document was to eliminate the ambiguities in the case of differences in the literature, and above all, to supplement existing data (mainly in the case of gas mixtures).

Subsequently, this document was used for other purposes than the selection of cylinder valve outlets, such as establishing flammability and oxidizing potential data for the classification and labelling of gases and gas mixtures.

This document is intended to be used under a variety of national regulatory regimes, but has been written so that it is suitable for the application of the UN Model Regulations and the UN-GHS[9].

Gas cylinders — Gases and gas mixtures — Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets

1 Scope

This document specifies methods for determining whether or not a gas or gas mixture is flammable in air and whether a gas or gas mixture is more or less oxidizing than air under atmospheric conditions.

This document is intended to be used for the classification of gases and gas mixtures including the selection of gas cylinder valve outlets.

This document does not cover the safe preparation of these mixtures under pressure and at temperatures other than ambient.

2 Normative references

There are no normative references in this document.

3 Terms, definitions, symbols and units

3.1 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp

3.1.1
gas or gas mixture flammable in air
gas or gas mixture that is ignitable in air at atmospheric pressure and a temperature of 20 °C

3.1.2
lower flammability limit in air
minimum content of a gas or gas mixture in a homogeneous mixture with air at which a flame just starts to propagate

Note 1 to entry: The lower flammability limit is determined at atmospheric conditions.

Note 2 to entry: The term “flammability limit”, as used in this document, is sometimes called “explosion limit”.

3.1.3
upper flammability limit in air
maximum content of a gas or gas mixture in a homogeneous mixture with air at which a flame just starts to propagate

Note 1 to entry: The upper flammability limit is determined at atmospheric conditions.

Note 2 to entry: The term “flammability limit”, as used in this document, is sometimes called “explosion limit”.

3.1.4
flammability range
range of concentration between the lower and upper flammability limits

Note 1 to entry: The term “flammability range”, as used in this document, is sometimes also called “explosion range”.

3.1.5
gas or gas mixture more oxidizing than air
gas or gas mixture that is able, at atmospheric pressure, to support the combustion more than a reference mixture consisting of 23,5 % oxygen in nitrogen

3.1.6
oxidizing power
OP
dimensionless number that compares the oxidizing capability of a gas or gas mixture to that of oxygen

Note 1 to entry: OP is calculated as the sum of the products of the mole fraction(s) of each oxidizing component times its coefficient of oxygen equivalency, C_i.

3.1.7
atmospheric conditions
standard pressure of 101,3 kPa at 20 °C

3.2 Symbols

A_i	molar fraction of the i^{th} flammable gas in a gas mixture, in %
B_k	molar fraction of the k^{th} inert gas in a gas mixture, in %
C_i	coefficient of oxygen equivalency
F_i	i^{th} flammable gas in a gas mixture
I_k	k^{th} inert gas in a gas mixture
n	number of flammable gases in a gas mixture
p	number of inert gases in a gas mixture
K_k	coefficient of equivalency of an inert gas relative to nitrogen (see Table 1)
A_i'	equivalent content of a flammable gas
L_i	lower flammability limit in air of a flammable gas
T_{ci}	maximum content of flammable gas which, when mixed with nitrogen, is not flammable in air, in %
x_i	molar fraction of the oxidizing component, in %
He	helium
Ar	argon
Ne	neon
Kr	krypton
Xe	xenon
N_2	nitrogen

H_2 hydrogen

O_2 oxygen

CO_2 carbon dioxide

SO_2 sulfur dioxide

N_2O nitrous oxide

SF_6 sulfur hexafluoride

CF_4 carbon tetrafluoride

C_3F_8 octafluoropropane

C_2HF_5 pentafluoroethane

CH_4 methane

3.3 Units

For the purposes of this document, all gas percentages (%) are given as molar fractions (mol. %) which are equivalent to volume fractions (vol. %) under normal atmospheric conditions.

4 Flammability of gases and gas mixtures in air

4.1 General

4.2 and 4.3 give a test method and a calculation method for determining whether a gas or gas mixture is flammable in air. This is used to determine a valve outlet for transportation or GHS classification.

The test method (given in 4.2) may be used in all cases but shall be used when T_{ci} (or L_i) values are not available.

The calculation method (given in 4.3) may only be used if reliable T_{ci} (or L_i) values are available.

4.5 gives a calculation method to determine the lower flammability limit of the flammable mixture determined in 4.3 and may be used for the GHS flammable gas categories.

In cases where the test result is different from that obtained by calculation, the test result shall take precedence.

The non-flammable mixtures defined by UN number shall overrule any classification done by calculation.

4.2 Test method

4.2.1 Key points concerning safety

Tests shall be carried out by trained and competent personnel working in accordance with authorized procedures (see also 4.2.4). The reaction tube and flowmeter shall be adequately screened to protect personnel in the event of an explosion. Personnel shall wear personal protective equipment including safety glasses. During the ignition sequence, the reaction tube shall be open to the atmosphere and isolated from the gas supply. Care shall also be taken during the analysis of the test gas or mixture.

4.2.2 Principle

The gas or gas mixture is mixed in the desired proportions with air. In the quiescent test mixture, an ignition is initiated using an electric spark and it is observed whether or not a flame propagates through the reaction tube.

4.2.3 Test apparatus and materials

4.2.3.1 General

The apparatus (see Figure 1) includes:

— a mixer;

— a tube in which the reaction takes place;

— an ignition system;

— a system of analysis to determine the test gas composition.

NOTE Alternative equivalent apparatus can be used, as described in standard test methods for the determination of flammability limits, e.g. EN 1839 and ASTM E681.

4.2.3.2 Preparation

4.2.3.2.1 Test gas

The test gas shall be prepared to represent the most flammable composition that can occur in the normal course of production. The criteria to be used in establishing the composition of the test gas are manufacturing tolerances, i.e. the test gas shall contain the highest concentration of flammable gases encountered in the normal manufacturing process and the moisture content shall be less than or equal to 0,01 %. The test gas shall be thoroughly mixed and carefully analysed to determine the exact composition.

4.2.3.2.2 Compressed air

The compressed air shall be analysed and the moisture content shall be less than or equal to 0,01 %.

4.2.3.2.3 Test gas/air mixture

The compressed air and the gas to be tested are mixed in a blender, controlling the flowrates. The air-flammable gas mixture shall be analysed using a chromatograph or a simple oxygen analyser and a flammable gas detector.

4.2.3.3 Reaction tube

The test vessel is an upright cylinder of thick glass (e.g. 5 mm) having a minimum inner diameter of 50 mm and a minimum height of 300 mm. The ignition electrodes are separated by a distance of 5 mm and are placed 50 mm to 60 mm above the bottom of the cylinder. The cylinder is fitted with a pressure-release opening. The apparatus shall be shielded to restrict any explosion damage.

4.2.3.4 Ignition system

A spark generator capable of supplying high voltage sparks (e.g. 15 kV, 30 mA, a.c.) with energy of 10 J shall be used. The spark gap (distance between the electrodes) shall be 5 mm, the spark duration 0,2 s to 0,5 s.

4.2.4 Procedure for determination of flammability

When carrying out flammability tests, care shall be taken to avoid explosion. This can be done by commencing the experimental work at a known “safe” concentration of 1 % test gas in air. Subsequently, the initial gas concentration can be increased in small steps by 1 % until ignition occurs.

Prior to each ignition attempt, the test vessel shall be purged with the test mixture. The purging volume shall be at least 10 times the volume of the test vessel. Then, an ignition is attempted with the induction spark when the test mixture is quiescent, and it is observed visually whether or not a flame detaches from the ignition source and propagates.

If a flame detachment and an upwards propagation of at least 100 mm is observed, the test substance shall be classified as flammable.

If the chemical structure of the gas indicates that it would be non-flammable and the composition of the stoichiometric mixture with air can be calculated, only mixtures in the range from 10 % (absolute) less than the stoichiometric composition to 10 % greater than this composition need to be tested in 1 % steps.

With mixtures containing hydrogen, the flame is almost colourless. In order to confirm the presence of such flames, the use of temperature-measuring probes is recommended [see Figure 1 a)].

4.2.5 Procedure for determination of flammability limits

Unlike at the determination of flammability in general, it is necessary to apply a different test procedure for determining flammability limits (*FL*). Using the same test apparatus, test gas preparation and criterion of ignition as described in 4.2.3 and 4.2.4, the characterization of flammability limits consists of determining the amount of test substance in air with which the test mixture no longer ignites. Close to the flammability limit, the incremental change of test substance content in air is selected such that it is almost 0,1 % by volume for $FL < 10$ % and 0,2 % by volume for $FL \geq 10$ %.

For safety reasons, the initial ignition tests are carried out using a test mixture with test substance content which, if possible, lies outside the expected explosion range.

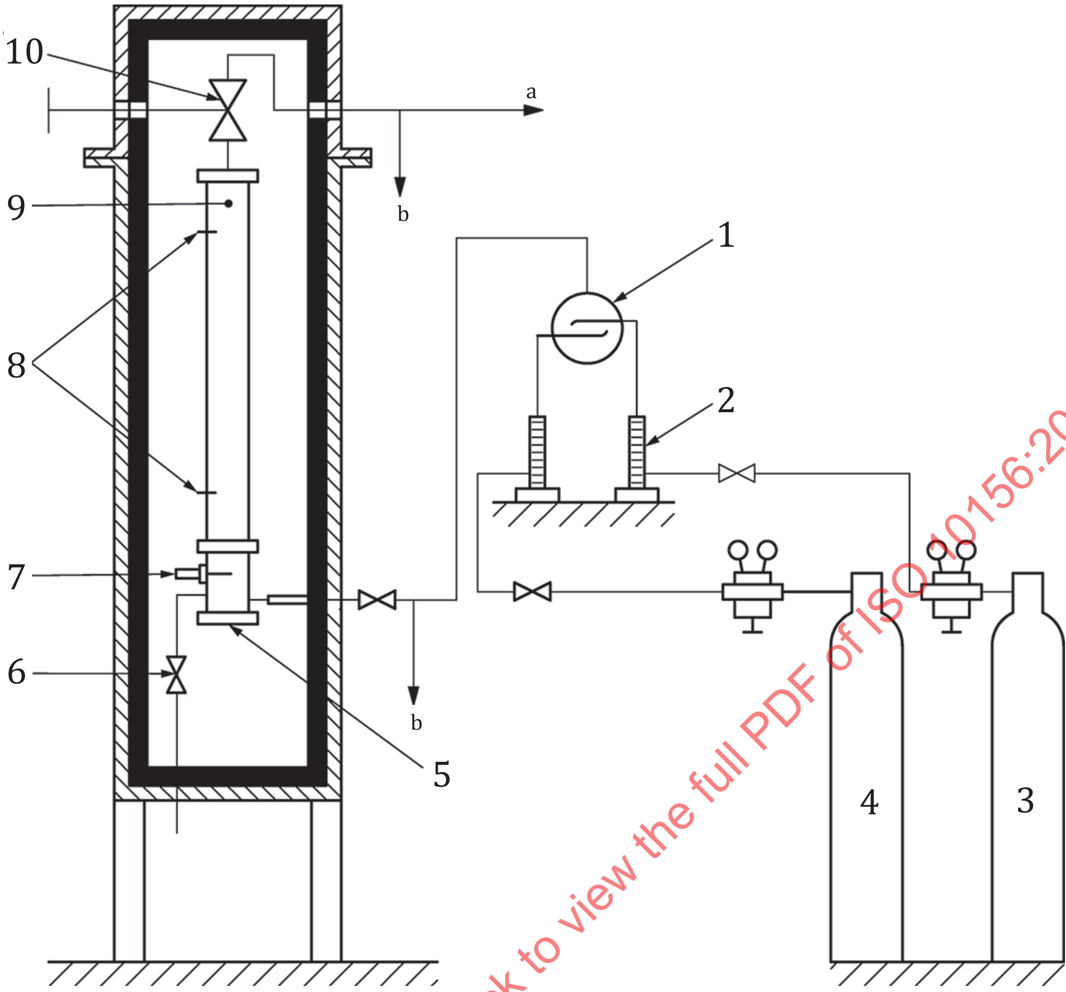
Prior to each ignition attempt, the test vessel is purged with the test mixture. The purging volume shall be at least 10 times the volume of the test vessel. When purging is complete, the inlet to the test vessel is sealed. The test mixture then bypasses the test vessel and flows directly into the exhaust system. An ignition is attempted using the induction spark under quiescent conditions. It is observed whether or not a flame detaches from the ignition source and propagates at least 100 mm.

If an ignition is observed, the test gas content in the test mixture is iteratively varied until no further flame detachment follows. The test mixture concentration at which an ignition just fails (just no flame detachment) shall be confirmed with four additional tests. The determination is terminated when with all five tests a flame detachment is not observed. If flame detachment does occur, the test gas content shall be further changed and the test gas content shall be reduced (lower flammability limit) or to be increased (upper flammability limit) by one increment. Again, the tests are carried out at the new test substance content.

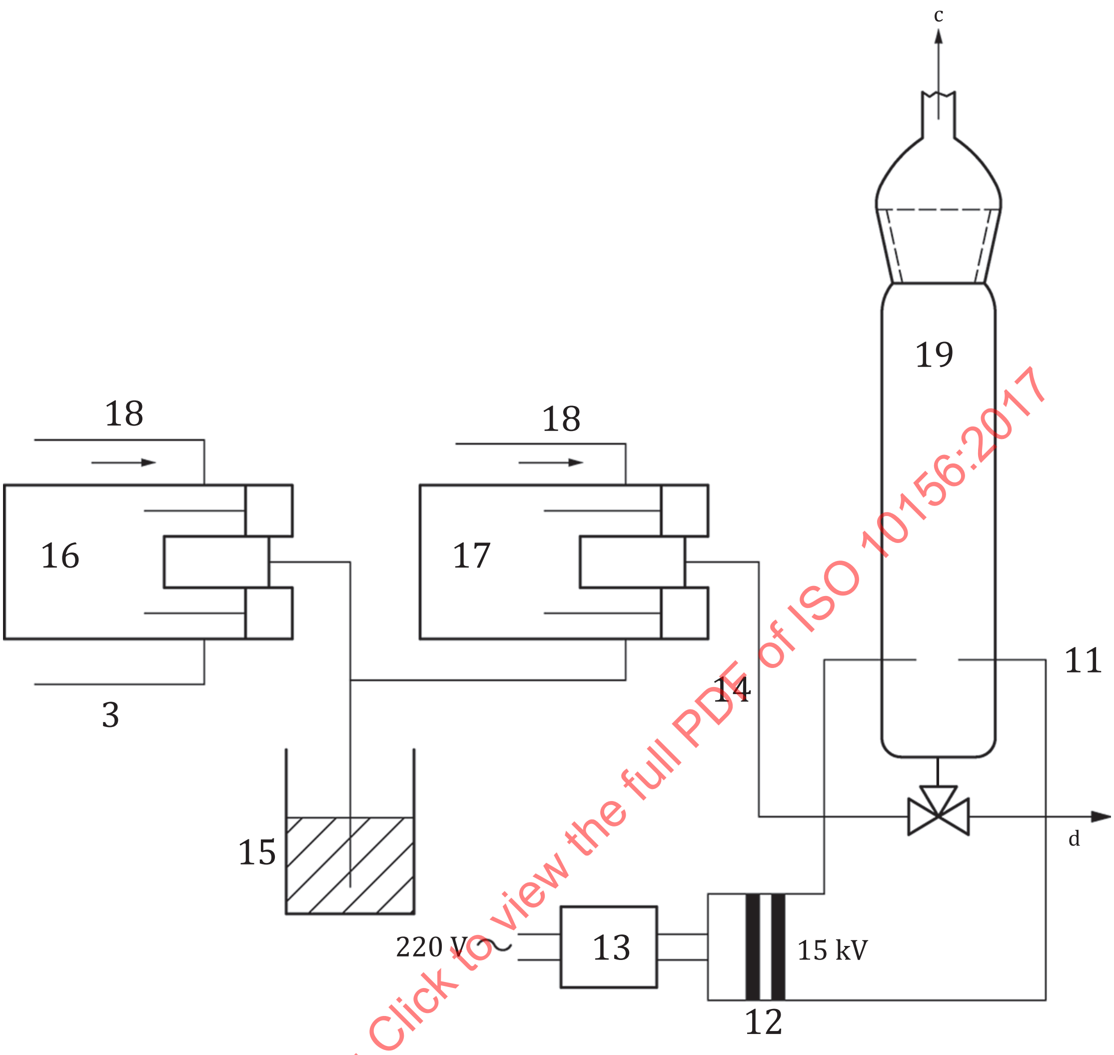
The flammability limit is the test gas concentration in mixture with air at which an ignition just fails.

4.2.6 Results for pure gases

A list of flammable gases is given in Table 2 together with T_{ci} values and L_i values. These values have been obtained using test equipment similar to that described in 4.2.3.



a) Apparatus using Pyrex tube and temperature-measuring probes



b) Apparatus suitable for testing a mixture of gases

Key

1 mixer
2 flowmeter
3 test gas
4 compressed air
5 safety device (pressure relief valve)
6 valve
7 spark plug
8 thermocouples
9 Pyrex tube, length 1 m, internal diameter 50 mm
10 valve
11 ignition electrodes
12 high-voltage transformer
13 timer switch
14 mixture containing *x* % test gas
15 low constant pressure device
16 metering pump 1, *x* %
17 metering pump 2, *y* %
18 air
19 mixture containing (*xy*/100) % test gas
a Gas mixture vented to atmosphere.
b Gas mixture analysed.
c Gas mixture analysed and vented to atmosphere.
d Gas mixture vented during test.

Figure 1 — Examples of apparatus for determination of flammability limits of gases at atmospheric pressure and ambient temperature

4.3 Calculation method for flammability of gas mixtures containing *n* flammable gases and *p* inert gases

The composition of a mixture of this kind can be expressed as follows:

$$A_1F_1 + \ldots + A_iF_i + \ldots + A_nF_n + B_1I_1 + \ldots + B_kI_k + \ldots + B_pI_p$$

The composition of the mixture is re-expressed in terms of an equivalent composition in which all the inert-gas fractions are converted into their nitrogen equivalent, using the coefficient of equivalency. K_k values are given in Table 1.

$$A_1F_1 + \ldots + A_iF_i + \ldots + A_nF_n + (K_1B_1 + \ldots + K_kB_k + \ldots + K_pB_p)N_2$$

Taking the sum of all the component gas fractions to be equal to 1, the expression for the composition is as shown in Formula (1):

$$\left(\sum_{i=1}^{n} A_iF_i + \sum_{k=1}^{p} K_kB_kN_2\right)\left(\frac{1}{\sum_{i=1}^{n} A_i + \sum_{k=1}^{p} K_kB_k}\right) \qquad (1)$$

where

$$\frac{A_i}{\sum_{i=1}^{n} A_i + \sum_{k=1}^{P} K_kB_k} = A_i'$$ is the equivalent flammable gas content.

The condition for the mixture not being flammable in air is shown in Formula (2):

$$\sum_{i=1}^{n} \frac{A_i'}{T_{ci}} 100 \leq 1 \qquad (2)$$

where T_{ci} is the maximum content of flammable gas or vapour, which, in a mixture with nitrogen, results in a composition which is not flammable in air. Values of T_{ci} are listed in Table 2 and Table 3 for gases and vapours.

Alternatively to the preceding formulae, the Formula (3) can be used, which does not require any intermediate steps:

$$\sum_{i=1}^{n} A_i\left(\frac{100}{T_{ci}} - 1\right) \leq \sum_{k=1}^{p} B_kK_k \qquad (3.)$$

Table 1 — Coefficients of equivalency, K_k, for inert gases relative to nitrogen

Gas	N_2	CO_2	He	Ar	Ne	Kr	Xe	SO_2	SF_6	CF_4	C_3F_8	C_2HF_5
K_k	1	1,5	0,9	0,55	0,7	0,5	0,5	1,5	4	2	1,5	3,5

NOTE These data are conservatively estimated based on experimental data and experiences within the gas industry.

For other non-flammable and non-oxidizing gases containing three atoms or more in their chemical formulae, the coefficient of equivalency K_k = 1,5 shall be used. Some types of non-flammable partial halogenated hydrocarbons, for example, the refrigerant R134a, can react partially with air and oxygen in the presence of flammable gases. For all mixtures containing more than 0,5 % non-flammable, partially halogenated hydrocarbons and flammable gases, the calculation method shall not be applied if the concentration of the flammable component exceeds 0,25 %.

Table 2 — T_{ci} and L_i values for the majority of flammable gases

Gas	CAS No.	UN No.	T_{ci} in %	L_i in %
Acetylene	74–86–2	3374	3,0	2,3
Ammonia	7664–41–7	1005	40,1	15,4
Arsine	7784–42–1	2188	3,9	3,9
Bromomethane	74–83–9	1062	13,9	8,6
1,2-Butadiene	590–19–2	1010	2,0	1,4
1,3-Butadiene	106–99–0	1010	2,0	1,4
n-Butane	106–97–8	1011	3,6	1,4
1-Butene	106–98–9	1012	3,3	1,5
cis-Butene	590–18–1	1012	3,3	1,5
trans-Butene	624–64–6	1012	3,3	1,5
Carbon monoxide	630–08–0	1016	15,2	10,9
Carbonyl sulfide	463–58–1	2204	6,5	6,5
Chlorodifluoroethane (R142b)	75–68–3	2517	26,4	6,3
Chloroethane	75–00–3	1037	5,8	3,6
Chlorotrifluoroethylene (R1113)	79–38–9	1082	7,4	4,6
Cyanogen	460–19–5	1026	3,9	3,9
Cyclobutane	287–23–0	2601	2,9	1,8
Cyclopropane	75–19–4	1027	3,4	2,4
Deuterium	7782–39–0	1957	6,7	6,7
Diborane	19287–45–7	1911	0,9	0,9
Dichlorosilane	4109–96–0	2189	2,5	2,5
Difluoroethane (R152a)	75–37–6	1030	8,7	4,0
Difluoroethylene (R1132a)	75–38–7	1959	6,6	4,7
Dimethyl ether	115–10–6	1033	3,8	2,7
Dimethylamine	124–40–3	1154	2,8	2,8
Dimethylpropane (neopentane)	463–82–1	2044	2,1	1,3
Ethane	74–84–0	1035	4,5	2,4
Ethyl methyl ether	540–67–0	1039	2,8	2,0
Ethylacetylene	107–00–6	2452	1,8	1,3
Ethylene	74–85–1	1962	4,1	2,4
Ethylene oxide	75–21–8	1040	4,8	2,6
Fluoroethane	353–36–6	2453	6,1	3,8
Fluoromethane	593–53–3	2454	9,0	5,6
Germane	7782–65–2	2192	1,0	1,0 (estimated)
Hydrogen	1333–74–0	1049	5,5	4,0
Hydrogen selenide	7783–07–5	2202	4,0	4,0
Hydrogen sulfide	7783–06–4	1053	8,9	3,9
Isobutane	75–28–5	1969	3,4	1,5
Isobutene	115–11–7	1055	4,0	1,6
Methane	74–82–8	1971	8,7	4,4
Methyl chloride	74–87–3	1063	12,3	7,6
Methyl mercaptan	74–93–1	1064	5,7	4,1
NOTE Values for other flammable gases can be found in IEC/TR 60079-20.				

Table 2 *(continued)*

Gas	CAS No.	UN No.	T_{ci} in %	L_i in %
Methyl nitrite	624–91–9	2455	5,3	5,3
Methyl silane	992–94–9	3161	1,3	1,3
Methylacetylene (propyne)	74–99–7	3161	2,5	1,8
Methylamine	74–89–5	1061	6,9	4,9
Methylbutene (3-methylbut-1-ene)	563–45–1	2561	2,4	1,5
Monoethylamine	75–04–7	1036	5,7	3,5
Phosphine	7803–51–2	2199	1,7	1,6
Propadiene	463–49–0	2200	2,7	1,9
Propane	74–98–6	1978	3,7	1,7
Propene	115–07–1	1077	4,2	1,8
Silane	7803–62–5	2203	1,0	1,4
Tetrafluoroethylene (R1114)	116–14–3	1081	10,5	10,5
Trifluoroethane (R143a)	420–46–2	2035	11,3	7,0
Trifluoroethylene (R1123)	359–11–5	1954	13,1	10,5
Trimethylamine	75–50–3	1083	3,2	2,0
Trimethylsilane	993–07–7	3161	1,3	1,3
Vinyl bromide	593–60–2	1085	9,0	5,6
Vinyl chloride	75–01–4	1086	6,1	3,8
Vinyl fluoride	75–02–5	1860	4,7	2,9
Vinyl methyl ether	107–25–5	1087	3,6	2,2
NOTE Values for other flammable gases can be found in IEC/TR 60079-20.				

Table 3 — T_{ci} and L_i values for the majority of flammable vapours

Vapour	CAS No.	UN No.	T_{ci} in %	L_i in %
Acetaldehyde	75–07–0	1088	6,5	4,0
Acetone	67–64–1	1090	4,0	2,5
Benzene	71–43–2	1114	2,3	1,2
Carbon disulfide	75–15–0	1131	1,3	0,6
Cyclohexane	110–82–7	1145	1,8	1,0
n-Decane	124–18–5	2247	1,1	0,7
Diethyl ether	60–29–7	1155	2,4	1,7
Dimethyl acetylene (2-butyne, crotonylene)	503–17–3	1144	2,0	1,4
2,2-Dimethylbutane (neohexane)	75–83–2	1208	1,9	1,2
n-Dodecane	112–40–3	—	1,0	0,6
Ethanol	64–17–5	1170	5,6	3,1
Ethyl acetate	141–78–6	1173	4,6	2,0
Ethyl chloride (Chloroethane)	75–00–3	1037	5,8	3,6
Ethyl formate	109–94–4	1089	3,8	2,7
n-Heptane	142–82–5	1206	1,3	0,8
n-Hexane	110–54–3	1208	2,3	1,0
NOTE Values for other flammable vapours can be found in IEC/TR 60079-20.				

Table 3 *(continued)*

Vapour	CAS No.	UN No.	T_{ci} in %	L_i in %
Hydrogen cyanide	74–90–8	1051	5,4	5,4
Isooctane (2,2,4-trimethylpentane)	540–84–1	1262	1,6	1,0
Isopentane (2-methylbutane)	78–78–4	1265	2,1	1,3
Lead tetraethyl (tetraethyllead)	78–00–2	1649	1,8	1,8
Methanol	67–56–1	1230	12,5	6,0
Methyl acetate	79–20–9	1231	5,0	3,1
Methyl ethyl ketone (butanone)	78–93–3	1193	2,4	1,5
Methyl formate	107–31–3	1243	8,1	5,0
Methylene chloride (Dichloromethane)	75–09–2	1592	21,0	13,0
Monochlorosilane	13465–78–6	2986	1,0	1,0 (estimated)
Nickel carbonyl (tetracarbonylnickel)	13463–39–3	1259	0,9	0,9
n-Nonane	111–84–2	1920	1,1	0,7
n-Octane	111–65–9	1262	1,3	0,8
n-Pentane	109–66–0	1265	1,8	1,1
Propyl formate	110–74–7	1281	4,6	2,1
Propylene oxide	75–56–9	1280	3,7	1,9
Toluene	108–88–3	1294	2,3	1,0
NOTE Values for other flammable vapours can be found in IEC/TR 60079-20.				

4.4 Examples

Example 1

Consider a mixture containing 7 % H_2 + 93 % CO_2.

Using the appropriate K_k value from Table 1, this mixture is equivalent to

$$7\ (H_2) + 1{,}5 \times 93\ (N_2)$$

or

$$7\ (H_2) + 139{,}5\ (N_2)$$

or, adjusting the sum of the molar fractions to 1,

$$4{,}78\ \%\ H_2 + 95{,}22\ \%\ N_2.$$

From Table 2, it can be seen that the T_{ci} value for H_2 is 5,5.

Since the ratio 4,78/5,5 (= 0,869) is less than 1, the mixture is not flammable in air.

Example 2

Consider a mixture comprising

$$2\ \%\ H_2 + 8\ \%\ CH_4 + 25\ \%\ Ar + 65\ \%\ He$$

Calculation steps:

Step 1: Convert the inert gases into their nitrogen equivalent using the coefficient of equivalency given in Table 1.

$$1 \times 2\ \% + 1 \times 8\ \% + 0{,}55 \times 25\ \% + 0{,}9 \times 65\ \%$$

Step 2: Adjust the contents of the components so that the sum is standardized to 1.

$$\frac{2\ \%}{82{,}25\ \%}+\frac{8\ \%}{82{,}25\ \%}+\frac{13{,}75\ \%}{82{,}25\ \%}+\frac{58{,}5\ \%}{82{,}25\ \%}$$

$$=0{,}024\,3+0{,}097\,3+0{,}167\,2+0{,}711\,2$$

Step 3: Calculate the relative flammability using the T_{ci} values given in Table 2 and compare the outcome to the criterion.

T_{ci} value for H_2 is 5,5.

T_{ci} value for CH_4 is 8,7.

$$\sum_{i=1}^{n}\frac{A'_i}{T_{ci}}100\le 1$$

$$\frac{A'_1}{T_{c1}}100+\frac{A'_2}{T_{c2}}100$$

$$=\frac{0{,}024\,3}{5{,}5}100+\frac{0{,}097\,3}{8{,}7}100=1{,}56$$

Since 1,56 > 1, the criterion for a non-flammable gas mixture is not fulfilled and this particular gas mixture is considered to be flammable.

Alternative step 3: Use the alternative, combined formula:

$$\sum_{i=1}^{n}A_i\left(\frac{100}{T_{ci}}-1\right)\le\sum_{k=1}^{p}K_kB_k$$

$$\sum_{i=1}^{n}A_i\left(\frac{100}{T_{ci}}-1\right)=2\left(\frac{100}{5{,}5}-1\right)+8\left(\frac{100}{8{,}7}-1\right)=118{,}3$$

$$\sum_{k=1}^{p}K_kB_k=0{,}55\cdot 25+0{,}9\cdot 65=72{,}25$$

Since 118 > 72,25, the criterion for a non-flammable gas mixture is not fulfilled and this particular gas mixture is considered to be flammable.

4.5 Calculation method for lower flammability limit of gas mixtures

4.5.1 General

For mixtures of flammable gases, Le Chatelier's formula is commonly used to predict lower flammability limits (L). The formula can be applied for mixtures being flammable but not for mixtures being potentially explosive (see 6.2)

Le Chatelier's formula cannot be used for calculation of upper explosion limits. Furthermore, it cannot be used for partial halogenated hydrocarbons or oxidizers other than air.

According to this formula, the lower flammability limit of the mixture (L_M) of fuel gas is given in Formula (4):

$$\frac{100}{L_M}=\frac{A_1}{L_1}+\frac{A_2}{L_2}+...+\frac{A_n}{L_n} \quad (4)$$

where L is the lower flammability limit in % and A is the molar fraction in % of the flammable gas in a mixture of n flammable gases. For classification purposes, Formula (4) can be modified as follows.

4.5.2 Mixtures of flammable gases and mixtures of flammable gases with nitrogen and/or air

Formula (5) can also be used in good approximation for mixtures of flammable gases, nitrogen and air:

$$L_M=\frac{100}{\sum_{i=1}^{n}\frac{A_i}{L_i}} \quad (5)$$

where L_i is the lower flammability limit of the flammable gas i and A_i is the molar fraction of flammable gas i in %, based on the mixture of which L_M is to be calculated.

4.5.3 Mixtures of flammable gases with inert gases other than nitrogen and air

Formula (6) takes into account the nitrogen equivalent (K_k) of inert gases other than nitrogen. A change in molar heat capacity of the air-inert mixture at L_M influences the necessary fuel concentration (heat of combustion) for flame propagation. L_M will be conservatively estimated because of the safety margin which is included in K_k values given in Table 1.

$$L_M=\frac{100}{\sum_{i=1}^{n}\frac{A_i}{L'_i}} \quad (6)$$

where L'_i is given by good approximation

$$L'_i=\frac{\left(100-L'_M-(1-K)\frac{\sum_{p=1}^{k}B_k}{\sum_{i=1}^{n}A_i}\times L'_M\right)}{(100-L'_M)}\times L_i$$

where L'_M is the lower flammability limit of a mixture consisting of only the flammable components calculated according to 4.5.2, K is the average of K_k, values of the inert gases weighted according to its molar fractions, A_i is the molar fraction of flammable gas i in % and B_k the inert fraction in % based on the mixture of which L_M *is* to be calculated.

Amounts of air or oxygen in the mixture to be calculated shall be regarded as inert gases in this case taking a K value of 1.

4.6 Examples

Example 1

Consider a mixture of two flammable gases, 80 % methane and 20 % ethane. Using Formula (5) with $L_{(CH_4)}=4{,}4\ \%$ and $L_{(C_2H_6)}=2{,}4\ \%$ (see Table 2), the lower flammability limit of mixture is:

$$L_M=\frac{100}{\sum_{i=1}^{n}\frac{A_i}{L_i}}=\frac{100}{\frac{80}{4{,}4}+\frac{20}{2{,}4}}=3{,}8\%$$

Example 2

Consider a mixture of a flammable gas, nitrogen and air, 48 % hydrogen and 50 % nitrogen and 2 % air. The mixture is flammable and not potentially explosive according to 6.2. Using Formula (5) with $L_{(H_2)} = 4,0\ \%$, the lower flammability of mixture is:

$$L_M = \frac{100}{\sum_{i=1}^{n} \frac{A_i}{L_i}} = \frac{100}{\frac{48}{4,0}} = 8,3\%$$

Example 3

Consider a mixture of 40 % methane and 60 % carbon dioxide. The mixture is flammable and not potentially explosive according to 6.2. Using Formula (6), $L'_M = L_{(CH_4)} = 4,4\ \%$ and $K_{(CO_2)} = K = 1,5\ \%$, the lower flammability of mixture is:

$$L'_i = \frac{\left(100 - L'_M - (1-K)\frac{\sum_{p=1}^{k} B_k}{\sum_{i=1}^{n} A_i} \times L'_M\right)}{(100 - L'_M)} \times L_i = \frac{\left(100 - 4,4 + 0,5 \times \frac{60}{40} \times 4,4\right)}{100 - 4,4} \times 4,4 = 4,55\ \%$$

$$L_M = \frac{100}{\sum_{i=1}^{n} \frac{A_i}{L'_i}} = \frac{100}{\frac{40}{4,55}} = 11,4\ \%$$

Example 4

Consider a mixture of 15 % hydrogen, 15 % methane, 30 % carbon dioxide, 35 % nitrogen and 5 % air. The mixture is flammable and not potentially explosive according to 6.2. Using Formula (6) with $L_{(H_2)} = 4,0\ \%$, $L_{(CH_4)} = 4,4\ \%$, $K_{(CO_2)} = 1,5\ \%$, $K_{(N_2)} = 1,0\ \%$ and $K_{(air)} = 1,0\ \%$, the lower flammability of the mixture is:

$$L'_M = \frac{100}{\sum_{i=1}^{n} \frac{A_i}{L_i}} = \frac{100}{\frac{50}{4,4} + \frac{50}{4,0}} = 4,2\ \%$$

$$K = \frac{30 \times 1,5 + 35 \times 1 + 5 \times 1}{70} = 1,21$$

$$L'_{CH_4} = \frac{\left(100 - L'_M - (1-K)\frac{\sum_{p=1}^{k} B_k}{\sum_{i=1}^{n} A_i} \times L'_M\right)}{(100 - L'_M)} \times L_i = \frac{\left(100 - 4,2 + 0,21 \times \frac{70}{30} \times 4,2\right)}{100 - 4,2} \times 4,4 = 4,5\ \%$$

$$L'_{H_2} = \frac{100 - 4,2 + 0,21 \times \frac{70}{30} \times 4,2}{100 - 4,2} \times 4,0 = 4,1\ \%$$

$$L_M = \frac{100}{\sum_{i=1}^{n} \frac{A_i}{L'_i}} = \frac{100}{\frac{15}{4,5} + \frac{15}{4,1}} = 14,3\ \%$$

4.7 Classification according to the Globally Harmonized System (GHS)

This document includes a test method for determination of flammability limits and a calculation method for the lower flammability limit (L_i). By use of these data, it is possible to classify mixtures containing flammable gases into either category 1 or category 2 according to the GHS (see Annex A).

The calculation method does not allow to calculate the upper flammability limit. Consequently, if the upper flammability limit is not determined by experimental testing, by default, flammable gas mixtures shall be classified as category 1.

5 Oxidizing power of gases and gas mixtures

5.1 General

5.2 and 5.3 give a test method and a calculation method for determining whether a gas or gas mixture will support combustion more than a reference mixture consisting of 23,5 % oxygen in nitrogen.

The test method (given in 5.2) may be used in all cases, but shall be used when coefficient of oxygen equivalency data are not available (see Table 4).

The calculation method (given in 5.3) may only be used when coefficient of oxygen equivalency data are available (see Table 4).

5.2 Test method

5.2.1 Key points concerning safety

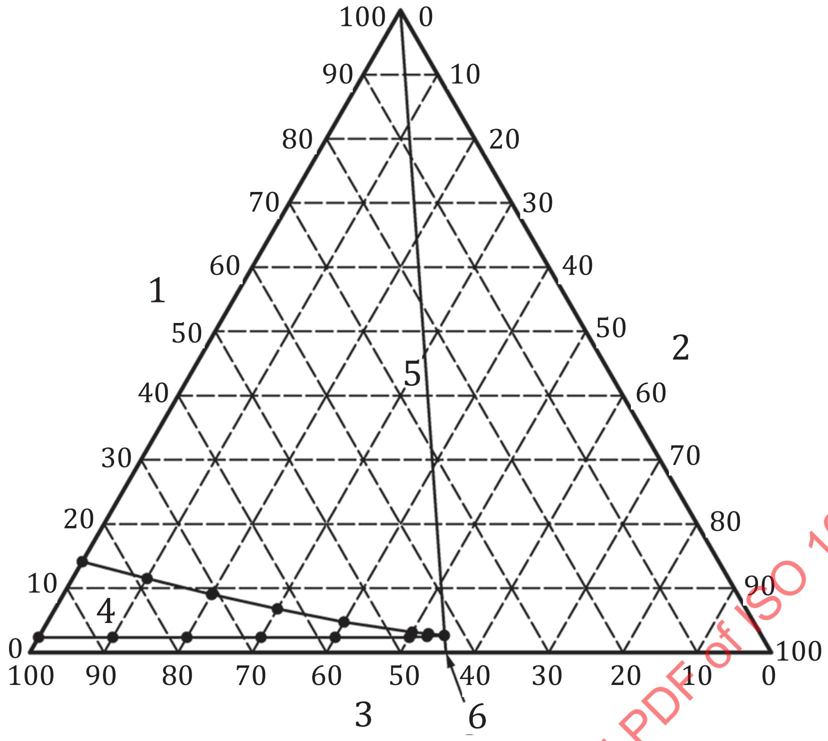
Tests shall be carried out by trained and competent personnel working in accordance with authorized procedures. The reaction tube and flowmeter shall be adequately screened to protect the personnel in the event of an explosion. Personnel shall wear safety glasses. During the ignition sequence, the reaction tube shall be open to the atmosphere and isolated from the gas supply. Care shall also be taken during the analysis of the test gas or mixture.

5.2.2 Principle

The gas or gas mixture to be evaluated (X) is mixed at a fixed ratio with nitrogen (N) to form a mixture (XN). That fixed ratio shall be the same as in the limiting mixture (NA) of nitrogen and air (A), which does not quite support combustion of the reference combustible, ethane (C) (see Figure 2).

By using the apparatus described in 5.2.3, the mixture (XN) is then mixed with increasing amounts of the reference combustible (C) to form test mixtures (XNC). By applying the procedure and criterion to determine flammability, it is observed if these test mixtures are flammable.

If any mixture of (XN) and (C) is flammable, the gas to be evaluated (X) is considered to be more oxidizing than air. If flammability is not observed in a range of combustible contents up to a maximum value (c_{max}), the gas to be evaluated is considered to be equal or less oxidizing than air.



Key

1 molar fraction of ethane, expressed in %

2 molar fraction of nitrogen, expressed in %

3 molar fraction of air, expressed in %

4 flammability range

5 line of constant ratio oxidizer/nitrogen

6 limiting oxidizer fraction (LOF) = 43,4 % air

Figure 2 — Flammability range of ethane/nitrogen/air at 20 °C and 101 kPa — Determination of limiting oxidizer fraction, which does not support the combustion of ethane

5.2.3 Test apparatus

5.2.3.1 Description

The apparatus (see Figure 3) includes:

— a closed test vessel with stirrer;

— an ignition system;

— two pressure measuring systems;

— a system for checking the test gas composition.

5.2.3.2 Test vessel

The test vessel shall be made of stainless steel and designed to withstand a maximum overpressure of at least 30 bar[1)]. The volume shall be at least 0,005 m^3. It can be either cylindrical or spherical. If a cylindrical vessel is used, the length to diameter ratio shall be 1. The vessel shall incorporate a stirrer and sufficient ports to enable filling, evacuation and purging.

1) 1 bar = 100 kPa (exactly).

The vessel shall be equipped with a suitable temperature measuring device.

5.2.3.3 Ignition system

A fusing wire igniter shall be used. This ignition device generates an electric arc by passing an electric current along a straight length of a NiCr-wire connecting two metal rods. The rods shall be of diameter ≥3 mm and shall be parallel to one another at a separation distance of (5 ± 1) mm. The diameter of wire shall be at least 0,05 mm and no more than 0,2 mm. The electrical power for melting this wire and generating the arc is supplied by an a.c. isolating transformer (power 0,7 kVA to 3,5 kVA, secondary voltage 230 V). The secondary winding of the transformer shall be switched to the rods by an electronic device allowing adjustment of the ignition energy between 10 J and 20 J. This can be achieved by phase-angle control of secondary voltage by thyristor switching elements.

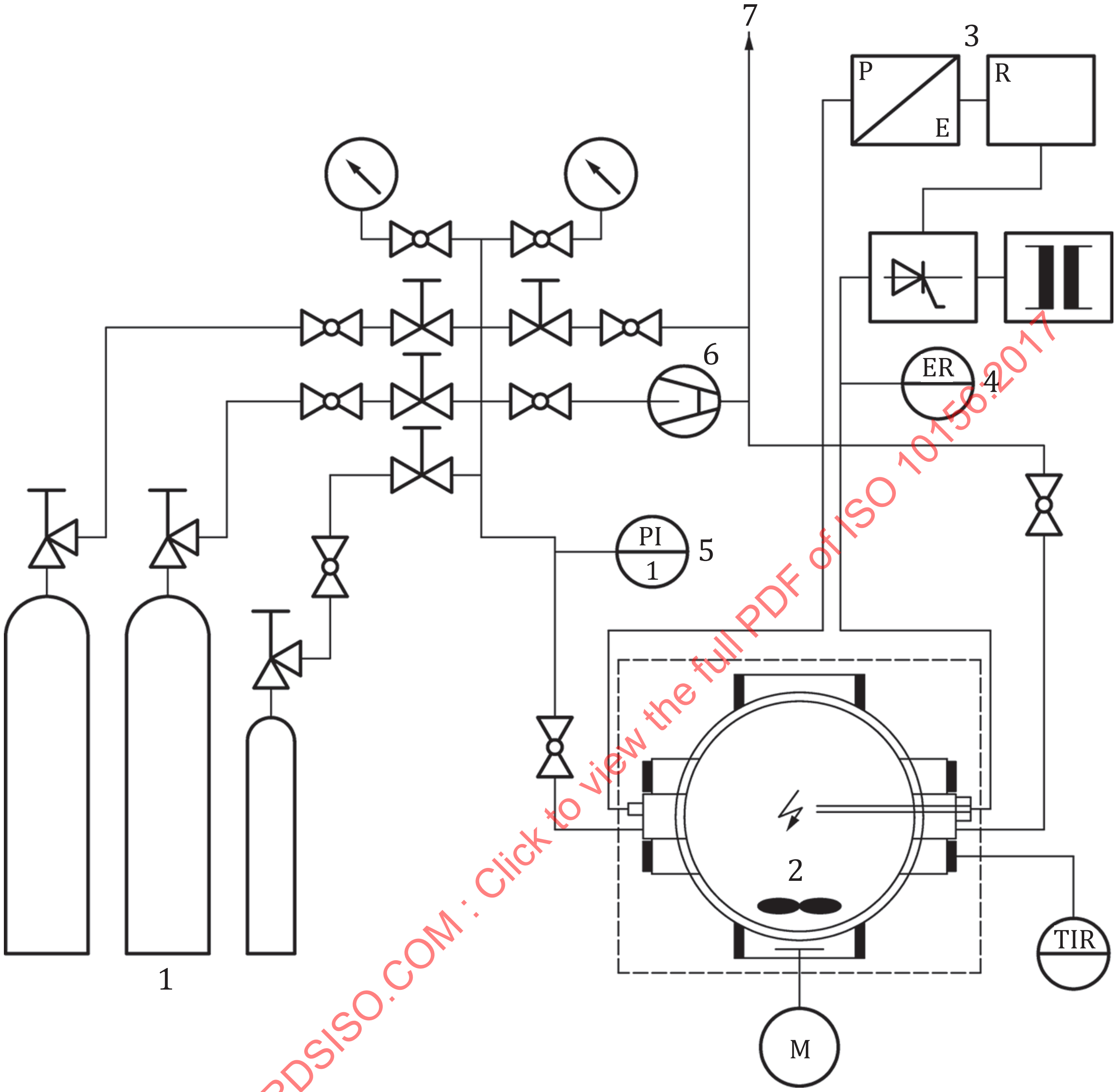
The fusing wire shall be positioned in the centre of the test vessel.

5.2.3.4 Pressure measuring system

The pressure measuring system for the explosion pressure consists of a pressure transducer, an amplifier and a data recording system. The pressure transducer and amplifier shall have a time resolution of at least 1 ms. The transducer shall be pressure resistant to at least a pressure of 30 bar with a measuring range of 10 bar. The pressure indication system for preparing the test mixtures according to the partial pressure method (pressure transducers or manometers) shall have a measuring range of 2 bar maximum. Both pressure measuring systems shall have an accuracy of 0,5 % full scale or better.

5.2.3.5 System for checking the test gas composition

The mixture (XN) or (XNC) shall be analysed using a gas chromatograph or another type of analyser.



Key

1 supply of pressurized gases
2 test vessel made of stainless steel with magnetic stirrer
3 recording unit for pressure rise inside the ignition vessel
4 fusing wire igniter and electronic control unit
5 pressure indication for preparing the mixtures
6 vacuum pump
7 waste gas disposal

Figure 3 — Example of apparatus for determination of oxidizing ability of gases and gas mixtures

5.2.3.6 Materials

Ethane of purity >99,5 % shall be used as reference combustible (C). The reason for using ethane as a reference fuel is because it has carbon-hydrogen bonds and also a carbon-carbon bond, as most of the combustible materials do, and flammability ranges of ethane with many oxidizing gases are already known.

The mixture (XN) shall consist of (38,5 ± 1) % gas-to-be-evaluated, with the remainder consisting of nitrogen of purity 99,995 %. (XN) can be prepared directly in the test vessel according to the partial pressure of each component. It is also admissible to produce a pressurized mixture (XN) in an evacuated gas cylinder by way of an additional metering device and to use this premixed gas for the subsequent procedure.

The mixture (XN), or one of the mixtures (XNC) when this mixture is directly made in the autoclave, shall be analysed.

The moisture content of gases shall be less than 0,01 % by volume. If for any reason this cannot be achieved (as might be the case for hygroscopic gases or unknown substances), this shall be indicated in the report.

5.2.4 Procedure

The tests are carried out at room temperature (20 ± 5) °C and atmospheric pressure (101,3 ± 3) kPa. The test mixtures (XNC) shall be prepared in the test vessel according to the partial pressures up to a final filling pressure of 1 bar. Ethane is added to the mixture (XN) step by step. For each step, an ignition is initiated and it is observed whether or not a reaction occurs. This reaction is indicated by a pressure rise after ignition of at least 10 % of initial pressure. The tests are started at a fraction of ethane of 1 %. If no reaction occurs, the percentage of ethane is increased by steps of 1 % until a reaction occurs or until the percentage of ethane is more than 20 %.

ATTENTION — There could be a risk of explosion when carrying out this test. Take special care when dealing with toxic and corrosive gases. Make personnel aware of the potential hazards and take the necessary precautions. The test apparatus should be installed in a laboratory fume cupboard.

Fuel gas and oxidants to be tested shall not be mixed together under pressure in gas cylinders except if performed by competent persons according to a well-proven procedure. This document does not attempt to clarify which oxidizing gas mixtures can be manufactured safely and successfully, since this is the responsibility of the mixture manufacturer using established practices and procedures for safety of personnel, equipment and surroundings.

5.2.5 Results

If reaction has been observed during the tests, the gas or gas mixture to be evaluated is more oxidizing than air.

5.3 Calculation method

5.3.1 Principle

To determine the OP of gas mixtures, the following calculation method is given.

A mixture is considered to be more oxidizing than air if the following condition is satisfied:

$$\sum_i x_i C_i > 23{,}5\,\%$$

In the above condition, the diluting effect of the inert gases other than nitrogen is not regarded. If a mixture to be evaluated contains such inert gases, the K_k factors shall be taken into consideration [see Formula (7)]:

$$\mathrm{OP} = \frac{\sum_{i=1}^{n} x_i C_i}{\sum_{i=1}^{n} x_i + \sum_{k=1}^{p} K_k B_k} \tag{7}$$

The coefficients of nitrogen equivalency, K, and molar fractions of the inert gases, B, are defined in this subclause and listed in Table 1.

Dry atmospheric air has an oxygen fraction of 20,95 %. For the purposes of this document, any mixture containing less than or equal to 23,5 % oxygen may be considered as non-oxidizing.

Example 1

5 % N_2O + 10 % O_2 + 85 % N_2

$$\mathrm{OP} = \sum x_i C_i = (0{,}05 \times 0{,}6) + (0{,}1 \times 1{,}0) = 0{,}13$$

Since 13 % < 23,5 %, the mixture is less oxidizing than air.

Example 2

20 % N_2O + 20 % O_2 + 40 % N_2 + 20 % CO_2

$$\mathrm{OP} = \frac{\sum_{i=1}^{n} x_i C_i}{\sum_{i=1}^{n} x_i + \sum_{k=1}^{p} K_k B_k} = \frac{(0{,}2 \times 0{,}6) + (0{,}2 \times 1{,}0)}{0{,}4 + (0{,}4 \times 1) + (0{,}2 \times 1{,}5)} = 0{,}29$$

Since 29 % > 23,5 %, this mixture shall be classified as more oxidizing than air.

5.3.2 C_i coefficients

The C_i coefficients of oxidizing gases were deduced from the explosion ranges of oxidizing gases in mixture with nitrogen and ethane. For the determination of C_i, it is necessary to consider the oxidizer fraction of the limiting ratio oxidizer/nitrogen (see Figure 2). This limiting oxidizer fraction (LOF) is inversely proportional to the wanted C_i coefficient [see Formula (8)]:

$$C_i = 9{,}07 \frac{1}{\mathrm{LOF}} \tag{8}$$

The C_i coefficient is specific to each oxidizing gas. By definition, the C_i of oxygen is 1,0.

The factor 9,07 was derived from the LOF value of air using the definition C_i (oxygen) = 1. Table 4 gives C_i values derived from experimental LOF[6]. For untested gases, C_i was given a conservative value of 40.

Table 4 — Coefficients of oxygen equivalency (C_i)

Gas/vapour	C_i coefficient
Bis-trifluoromethylperoxide	40[a]
Bromine pentafluoride	40[a]
Bromine trifluoride	40[a]
Chlorine	0,7
Chlorine pentafluoride	40[a]
Chlorine trifluoride	40[a]
Fluorine	40[a]
Iodine pentafluoride	40[a]
Nitric oxide	0,3
Nitrogen dioxide	1[b]
Nitrogen trifluoride	1,6
Nitrogen trioxide	40[a]
Nitrous oxide	0,6
Oxygen difluoride	40[a]
Ozone	40[a]
Tetrafluorohydrazine	40[a]

[a] This conservative value has been assigned to untested oxidizing gases and vapours.

[b] Derived from nitric oxide and nitrogen trifluoride.

6 Mixtures containing oxygen and flammable gases

6.1 General

NOTE 1 Mixtures of flammable gases and oxidizing gases other than oxygen are not considered.

NOTE 2 Mixtures of partially halogenated hydrocarbons, which are non-flammable in air at ambient pressure and temperature, can become flammable when mixed with air at higher pressures and temperatures or with oxidizers with an oxidizing potential greater than air.

For calculation of $T_{ci,F}$ the nitrogen equivalency of the mixtures shall be taken into account.

When a mixture contains flammable and oxidizing gases, it can be classified as one of the following four categories (see also Figure 4).

— A) Non-flammable and non-oxidizing, if the oxygen content is less than or equal to 23,5 % and the content of the flammable gases is below the $T_{ci,F}$ or L_i (see 6.2).

— B) Oxidizing, if the oxygen content is more than 23,5 % and the content of the flammable gases is below the L_i.

— C) Flammable, if the content of the flammable gases is more than the $T_{ci,F}$ and more than the L_i (see 6.2).

— D) Potentially explosive, if the oxygen content is greater than the limiting oxygen concentration (LOC) and the content of the flammable gases is more than the L_i and the $T_{ci,F}$.

For risk assessment and avoidance of explosive gas mixtures, the LOCs are given in Table 5. LOC is the maximum oxygen concentration in any mixtures of a flammable substance, air or inert gas, at