INTERNATIONAL STANDARD

ISO 10156

Third edition
2010-04-01

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

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

Reference number
ISO 10156:2010(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

COPYRIGHT PROTECTED DOCUMENT

© ISO 2010

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

Foreword iv
Introduction v
1 Scope 1
2 Terms, definitions, symbols and units 1
2.1 Terms and definitions 1
2.2 Symbols 2
2.3 Units 3
3 Flammability of gases and gas mixtures in air 3
3.1 General 3
3.2 Test method 3
3.2.1 Key points concerning safety 3
3.2.2 Principle 3
3.2.3 Test apparatus and materials 3
3.2.4 Procedure 4
3.2.5 Results for pure gases 4
3.3 Calculation method for mixtures containing n flammable gases and p inert gases 7
3.4 Examples 11
3.5 Classification according to the Globally Harmonized System (GHS) 12
4 Oxidizing power of gases and gas mixtures 12
4.1 General 12
4.2 Test method 12
4.2.1 Key points concerning safety 12
4.2.2 Principle 12
4.2.3 Test apparatus 13
4.2.4 Procedure 16
4.2.5 Results 16
4.3 Calculation method 16
4.3.1 Principle 16
4.3.2 C_i coefficients 17
5 Mixtures containing oxygen and flammable gases 18
5.1 General 18
5.2 Basis of flammability classification 20
5.3 Examples 22
Annex A (informative) Classification according to the Globally Harmonized System (GHS) 24
Bibliography 25

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 10156 was prepared by Technical Committee ISO/TC 58, *Gas cylinders*, Subcommittee SC 2, *Cylinder fittings*.

This third edition of ISO 10156 cancels and replaces ISO 10156:1996 and ISO 10156-2:2005.

It gives updated data for flammability and oxidizing ability.

Introduction

ISO 5145 [1] and other related standards establish practical criteria for the determination of outlet connections of cylinder valves. These criteria are based on certain physical and chemical properties of the gases. In particular, the flammability in air and the oxidizing ability are considered.

One of the potential complications that prompted the development of this International Standard is that whilst 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 International Standard 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 International Standard was used for other purposes than the selection of cylinder valve outlets, such as establishing flammability and oxidizing potential data for labelling according to international transport regulations and dangerous substances regulations, under the umbrella of the Globally Harmonized System (GHS).

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

1 Scope

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

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

2 Terms, definitions, symbols and units

2.1 Terms and definitions

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

2.1.1
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

2.1.2
lower flammability limit in air
minimum content of a gas or gas mixture in an homogeneous mixture with air at which a flame just starts to propagate

NOTE 1 The lower flammability limit is determined at atmospheric conditions.

NOTE 2 The term “flammability limit”, as used in this International Standard, is sometimes called “explosion limit”.

2.1.3
upper flammability limit in air
maximum content of a gas or gas mixture in an homogeneous mixture with air at which a flame just starts to propagate

NOTE 1 The upper flammability limit is determined at atmospheric conditions.

NOTE 2 The term “flammability limit”, as used in this International Standard, is sometimes called “explosion limit”.

2.1.4
flammability range
range of concentration between the lower and upper flammability limits

NOTE The term “flammability range”, as used in this International Standard, is sometimes also called “explosion range”.

2.1.5
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 oxidizer consisting of 23,5 % oxygen in nitrogen

2.1.6
oxidizing power
OP
oxidizing potential
dimensionless number that compares the oxidizing capability of a gas mixture to that of oxygen

NOTE 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.

2.2 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
CH_4	methane

2.3 Units

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

3 Flammability of gases and gas mixtures in air

3.1 General

Subclauses 3.2 and 3.3 give a test method and a calculation method for determining whether a gas or gas mixture is flammable in air.

The test method (given in 3.2) 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 3.3) may only be used if reliable T_{ci} (or L_i) values are available.

3.2 Test method

3.2.1 Key points concerning safety

Tests shall be carried out by trained and competent personnel working in accordance with authorized procedures (see also 3.2.4). 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.

3.2.2 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.

3.2.3 Test apparatus and materials

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 may be used, as described in standard test methods for the determination of explosion limits, e.g. EN 1839 [2] and ASTM E 681 [3].

3.2.3.1 Preparation

3.2.3.1.1 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.

3.2.3.1.2 Compressed air

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

3.2.3.1.3 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.

3.2.3.2 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.

3.2.3.3 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.

3.2.4 Procedure

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 ten 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.

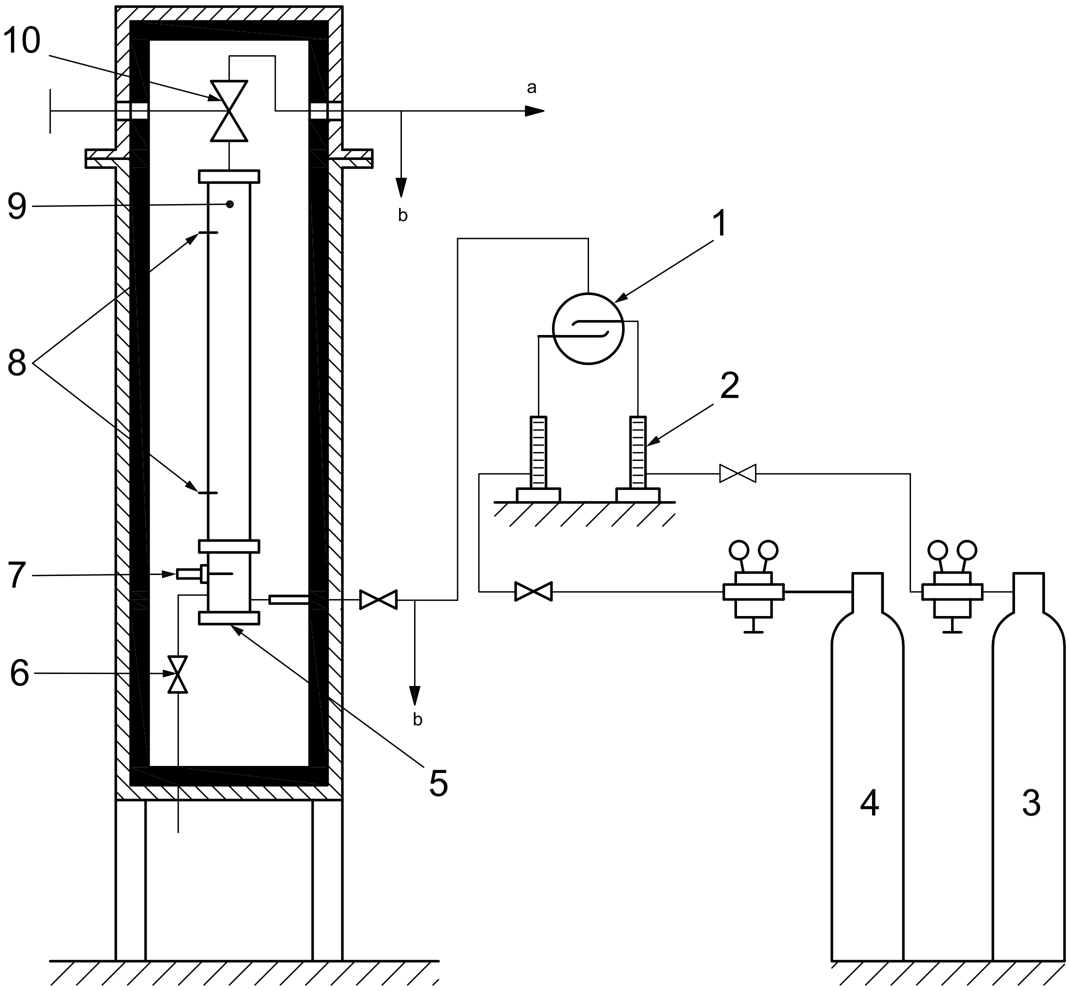
If a flame detachment and an upwards propagation of at least 100 mm is observed, the test substance shall be classified as flammable.

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 be tested in 1 % steps.

NOTE 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 1a)].

3.2.5 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 3.2.3.



a) Apparatus using Pyrex tube and temperature-measuring probes

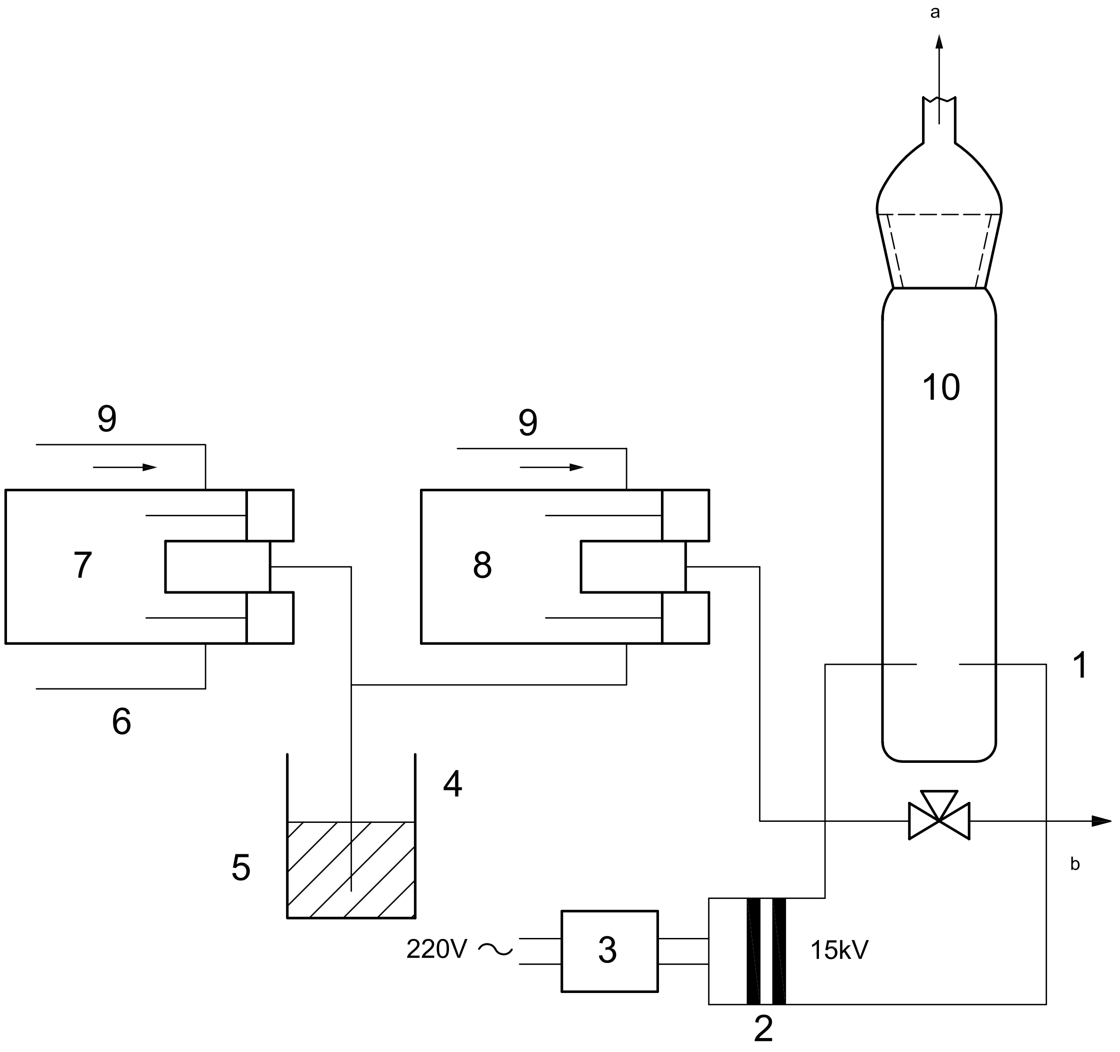
Key

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

[a] Gas mixture vented to atmosphere.

[b] Gas mixture analysed.

Figure 1 (*continued*)



b) Apparatus suitable for testing a mixture of gases

Key

1 ignition electrodes
2 high-voltage transformer
3 timer switch
4 mixture containing x % test gas
5 buffer vessel
6 test gas
7 metering pump 1, x %
8 metering pump 2, y %
9 air
10 mixture containing (xy/100)% test gas

[a] Gas mixture analysed and vented to atmosphere.

[b] Gas mixture vented during test.

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

3.3 Calculation method for 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:

$$A_1F_1 + \ldots + A_iF_i + \ldots + A_nF_n + (K_1B_1 + \ldots + K_kB_k + \ldots + K_pB_p)\text{N}_2$$

Taking the sum of all the component gas fractions to be equal to 1, the expression for the composition becomes:

$$\left(\sum_{i=1}^{n} A_iF_i + \sum_{k=1}^{p} K_kB_k\text{N}_2\right)\left(\frac{1}{\sum_{i=1}^{n} A_i + \sum_{k=1}^{p} K_kB_k}\right)$$

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

$$\sum_{i=1}^{n} \frac{A_i'}{T_{\text{ci}}} 100 \leqslant 1$$

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 Tables 2a) and 2b) for gases and vapours.

Alternatively to the preceding equations, the following equation can be used, which does not require any intermediate steps:

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

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
K_k	1	1,5	0,9	0,55	0,7	0,5	0,5	1,5	4	2	1,5
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 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 %. NOTE These data are conservatively estimated based on experimental data and experiences within the gas industry.											

Table 2 — T_{ci} and L_i values of flammable gases and vapours

a) Flammability data 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-Butenes	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

a) (*continued*)

Gas	**CAS No.**	**UN No.**	T_{ci} **in** %	L_i **in** %
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
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	1,0 (estimated)
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 [4].				

b) Flammability data 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 disulphide	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

b) (*continued*)

Vapour	CAS No.	UN No.	T_{ci} in %	L_i in %
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
Hydrogen cyanide	74-90-8	1051	5,4	5,4
Isooctane (2,2,4-trimethylpentane)	540-84-1	1262	1,6	1,0
Isopentan (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].

3.4 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.

$$\frac{2\ \%}{82{,}25\ \%} + \frac{8\ \%}{82{,}25\ \%} + \frac{13{,}75\ \%}{82{,}25\ \%} + \frac{58{,}5\ \%}{82{,}25\ \%}$$
$$= 0{,}024\ 3 + 0{,}097\ 3 + 0{,}878\ 4$$

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

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

$$\frac{A'_1}{T_{\text{c1}}} 100 + \frac{A'_2}{T_{\text{c2}}} 100$$
$$= \frac{0{,}024\ 3}{5{,}5} 100 + \frac{0{,}097\ 3}{8{,}7} 100 = 1{,}56$$

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

$$\sum_{i=1}^{n} \frac{A_i'}{T_{\mathrm{ci}}} \left(\frac{100}{T_{\mathrm{ci}}} - 1 \right) \leqslant \sum_{k=1}^{p} KkBk$$

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

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

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.

3.5 Classification according to the Globally Harmonized System (GHS)

This International Standard does not include methods to classify flammable gas mixtures into either category 1 or category 2 according to the GHS (see Annex A). Consequently, all mixtures containing flammable gases or flammable liquids as components and meeting the criteria of the testing method or the calculation method should be classified as category 1.

4 Oxidizing power of gases and gas mixtures

4.1 General

Subclauses 4.2 and 4.3 give a test method and a calculation method for determining whether a gas or gas mixture will support combustion more than a reference oxidizer consisting of 23,5 % oxygen in nitrogen.

NOTE Such gases are called “highly oxidizing” in this International Standard but are called “oxidizing” in the Globally Harmonized System (GHS).

The test method (given in 4.2) may be used in all cases, but shall be used when coefficient of oxygen equivalency data are not available (see Table 3).

The calculation method (given in 4.3) may only be used when coefficient of oxygen equivalency data are available (see Table 3).

4.2 Test method

4.2.1 Key points concerning safety

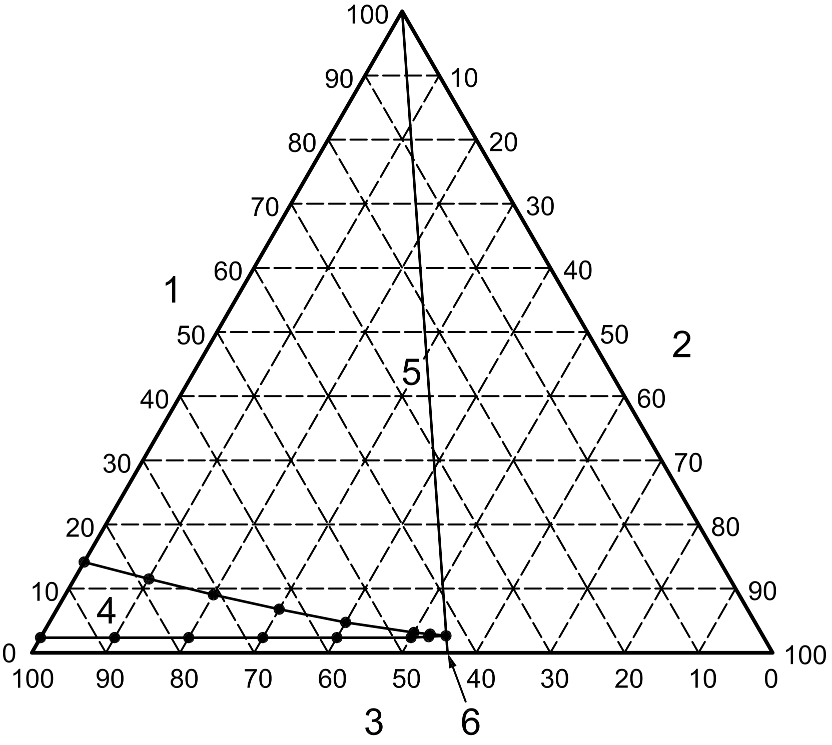
Tests shall be carried out by trained and competent personnel working in accordance with authorized procedures. The reaction tube and flowmeter shall be adequately screened to protect the personnel in the event of an explosion. Personnel shall wear safety glasses. During the ignition sequence, the reaction 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.

4.2.2 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 4.2.3, 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

4.2.3 Test apparatus

4.2.3.1 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.

4.2.3.2 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, evacuating and purging.

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

4.2.3.3 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 $\geqslant$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.

4.2.3.4 Pressure measuring system

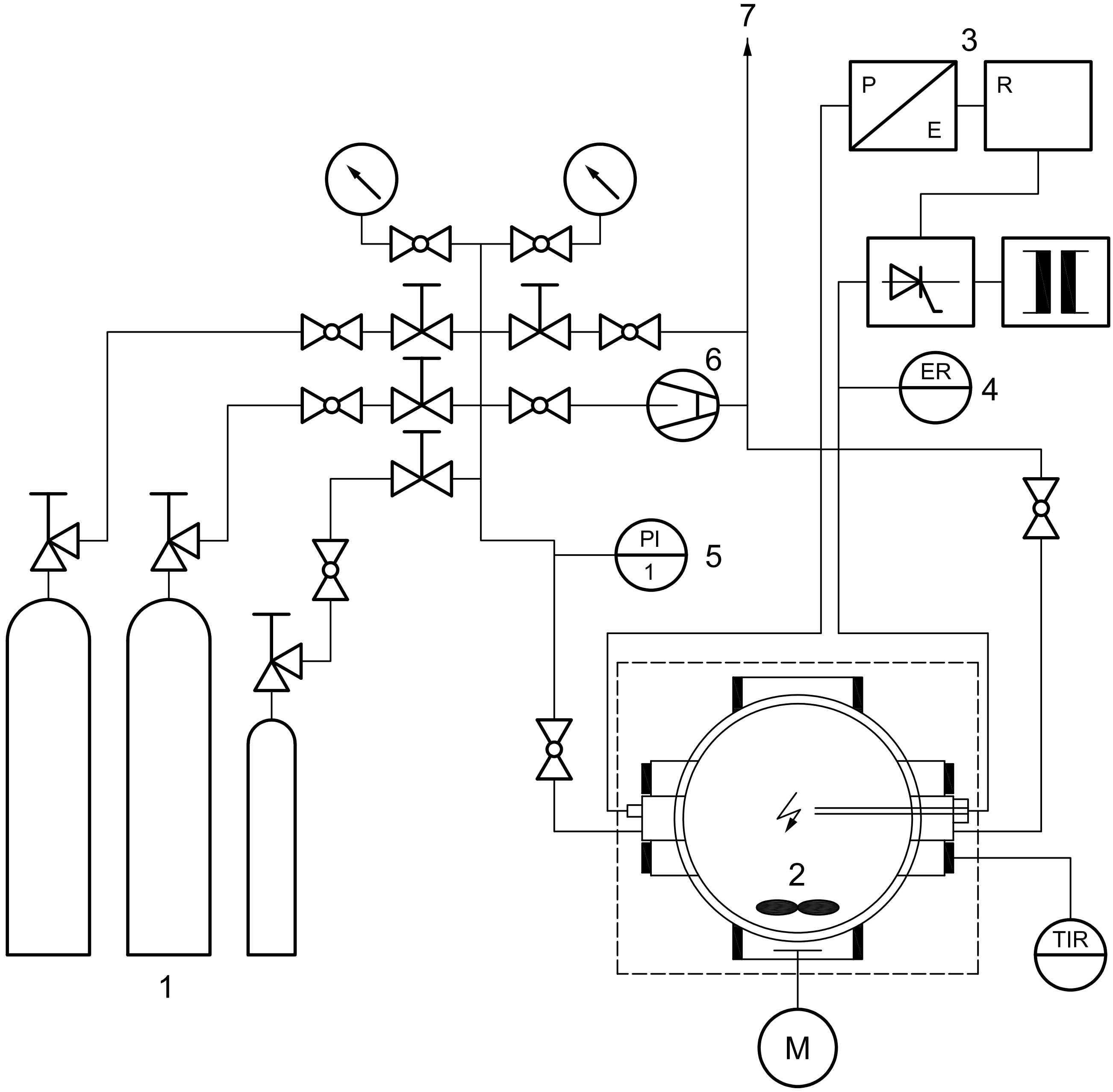
The pressure measuring system for the explosion pressure consists of a pressure transducer, an amplifier and a data recording system. The pressure transducer and amplifier shall have a time resolution of at least 1 ms. The transducer shall be pressure resistant to at least a pressure of 30 bar with a 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.

4.2.3.5 System for checking the test gas composition

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

---

1) 1 bar = 100 kPa (exactly).



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

4.2.3.6 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.

4.2.4 Procedure

The tests are carried out at room temperature and atmospheric pressure. 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 International Standard 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.

4.2.5 Results

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

4.3 Calculation method

4.3.1 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 formula, 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.

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

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

Dry atmospheric air has an oxygen fraction of 20,95 %. For the purposes of this International Standard, 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

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

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

Example 2

20 % N_2O + 20 % O_2 + 40 % N2 + 20 % CO_2

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

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

4.3.2 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.

$$C_i = 9{,}07 \frac{1}{\text{LOF}}$$

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 3 gives C_i values derived from experimental LOF [5]. For untested gases, C_i was given a conservative value of 40.

Table 3 — 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.

5 Mixtures containing oxygen and flammable gases

5.1 General

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

NOTE 2 Mixtures of partially halogenated hydrocarbons, that 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.

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

- Non flammable and non oxidizing, if the oxygen content is less than or equal to 23,5 % and the content of the flammable gases below the $T_{\text{ci,F}}$ or L_i (see 5.2).
- Oxidizing, if the oxygen content is more than 23,5 % and the content of the flammable gases below the L_i.
- Flammable, if the content of the flammable gases is more than the $T_{\text{ci,F}}$ and more than the L_i (see 5.2).
- 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.

For risk assessment and avoidance of explosive gas mixtures, the LOCs are given in Table 4. LOC is the maximum oxygen concentration in any mixtures of a flammable substance, air or inert gas, at atmospheric conditions, in which an explosion would not occur. LOCs are usually expressed as molar or volume fractions.

NOTE 3 The values given in Table 4 are only valid at atmospheric pressures; see also Reference [4].

Table 4 — Limiting oxygen concentrations (LOCs) of some flammable gases

Flammable substances	**LOC** % O_2
Ammonia	12,2
Benzene	8,5
n-Butane	9,6
1-Butene	9,7
Carbon monoxide	4,7
Carbon sulfide	4,6
Dimethyl ether	8,5
Ethane	8,8
Ethanol	8,5
Ethylene	7,6
n-Hexane	9,1
Hydrogen	4,3
Hydrogen sulfide	9,1
Isobutane	10,3
Isobutylene	10,6
Methane	11,0
Methanol	8,1
n-Pentane	9,3
Propane	9,8
1-Propanol	9,3
2-Propanol	8,7
Propylene	9,3
Propylene oxide	7,7
For flammable substances not listed here, a conservative value of 2 % shall be used.	

LOC corresponds to non-explosive gas mixture consisting of a flammable gas, air and nitrogen as inert gas at atmospheric pressure and ambient temperature.

5.2 Basis of flammability classification

A mixture containing flammable and oxidizing gases is classified as flammable if it meets both of the following conditions:

a) flammable gas concentration $(A_i) \geqslant L_i$;

b) flammable gas concentration $(A_i) > T_{\mathrm{ci,F}}$.

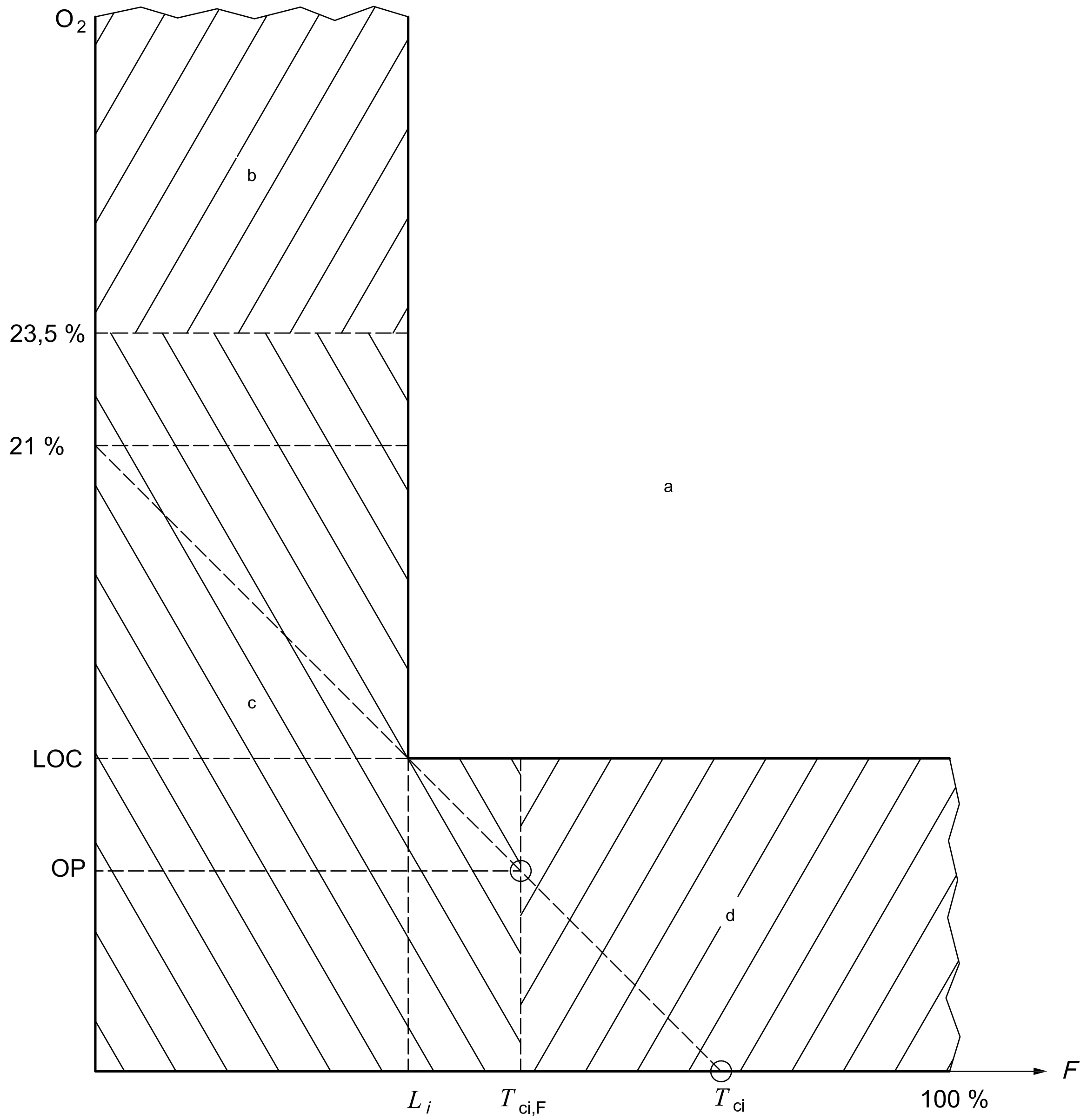
$T_{\mathrm{ci,F}}$ is calculated from the following formula:

$$T_{\mathrm{ci(flamox)}} = T_{\mathrm{ci}} \times (1 - x_{\mathrm{o}} / 21\%)$$

where x_{o} is the oxygen concentration, and is < 21 %.

The basis of the classification is shown in Figure 4. The line from T_{ci} to 21 % oxygen concentration shows the blending of a limiting mixture (highest non-flammable concentration of flammable gas in nitrogen) with air.

If a mixture has a low oxygen concentration, then the limiting case is on the same line, but starts off a little higher, going from the circle to 21% O_2. The corresponding $T_{\mathrm{ci,F}}$ is determined by projecting down to the flammable gas axis.



Key

F	concentration of flammable gas, expressed in %
O_2	concentration of oxygen, expressed in %

[a] Potentially explosive.

[b] Oxidizing.

[c] Non flammable and non oxidizing.

[d] Flammable.

Figure 4 — Classification basis

5.3 Examples

Example 1

Single flammable gas, inert gas (nitrogen)	5 % H_2, 3% O_2, 92 % N_2
Numerical	Flammable gas concentration = 5 % $L_i = 4$ % $T_{\mathrm{ci}} = 5{,}5$ % $x_{\mathrm{o}} = 3$ % $T_{\mathrm{ci,F}} = T_{\mathrm{ci}} \times [1 - (x_{\mathrm{o}}/21)] = 5{,}5 \times [1 - (3/21)] = 4{,}71$ %
Condition 1	Flammable gas concentration 5 % $\geqslant L_i$ 4 % = TRUE
Condition 2	Flammable gas concentration 5 % $> T_{\mathrm{ci,F}}$ 4,71 % = TRUE
Classification	Both conditions are true, so the mixture is flammable.

Example 2

Multiple flammable gases, inert gas (nitrogen)	2 % H_2, 1 % CH_4, 13 % O_2, 84 % N_2
In this example, the lower flammability limit and highest non-flammable concentration of a mixture of flammable gases is calculated directly using the formula of Le Chatelier. $L_{\mathrm{m}} = \dfrac{\sum A_i}{\sum \left(\dfrac{A}{L} \right)_i}$ and $T_{\mathrm{m}} = \dfrac{\sum A_i}{\sum \left(\dfrac{A}{T_{\mathrm{c}}} \right)_i}$	
Numerical	Flammable gas concentration = 2 % + 1 % = 3 % $L_{\mathrm{m}} = (2 + 1) / [(2/4) + (1/4{,}4)] = 4{,}12$ % $T_{\mathrm{c,m}} = (2 + 1) / [(2/5{,}5) + (1/8{,}7)] = 6{,}27$ % $x_{\mathrm{o}} = 13$ % $T_{\mathrm{ci,F}} = T_{\mathrm{c,m}} \times [1 - (x_{\mathrm{o}}/21)] = 6{,}27 \times [1 - (13/21)] = 2{,}39$ %
Condition 1	Flammable gas concentration 3 % $\geqslant L_{\mathrm{m}}$ 4,12 % = FALSE
Condition 2	Flammable gas concentration 3 % $> T_{\mathrm{ci,F}}$ 2,39 % = TRUE
Classification	Both conditions are not met, so the mixture is not flammable.

Example 3

Single flammable gas, other inert gases	10 % CO, 5 % O_2, 10 % N_2, 20 % CO_2, 25 % Ar, 30 % Ne
This example features inert gases with different inerting equivalencies to nitrogen. The molar fractions of those inert gases are multiplied by their K_k values from Table 1. The relative volumes of flammable gas, oxidant and equivalent nitrogen are then adjusted (normalized) to a total of 100 %.	
Numerical	Normalization factor, $F = \dfrac{100}{100 + \sum_{k=1}^{p}(K_k - 1)B_k}$ and $F = 100/[100 + (20 \times 0{,}5 - 25 \times 0{,}45 - 30 \times 0{,}3)] = 1{,}114$ Flammable gas concentration = 10 × 1,114 = 11,14 % $L_i = 10{,}9$ % $T_{\text{ci}} = 15{,}2$ % OP = 5 % × 1,114 = 5,57 % $T_{\text{ci,F}} = T_{\text{ci}} \times (1 - \text{OP}/21) = 15{,}2 \times (1 - 5{,}57/21) = 11{,}17$ %
Condition 1	Flammable gas concentration 11,14 % $\geqslant L_i$ 10,9 % = TRUE
Condition 2	Flammable gas concentration 11,14 % $> T_{\text{ci,F}}$ 11,17 % = FALSE
Classification	Both conditions are not met, so the mixture is not flammable.

Annex A
(informative)

Classification according to the Globally Harmonized System (GHS)

The GHS distinguishes two categories of flammable gases. See Table A.1

Table A.1 — Criteria for flammable gases

Category	Criteria
1	Gases that, at 20 °C and at 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 flammability range with air of at least 12 percentage points regardless of the lower flammability limit.
2	Gases, other than those of category 1, that at 20 °C and at a standard pressure of 101,3 kPa have a flammability range while mixed in air.

The majority of flammable gases are classified under category 1; only a few gases (e.g. ammonia) are classified under category 2.

The test methods and the calculation methods given in this International Standard do not cover the determination of flammability limits or flammability range of gaseous mixtures.

Bibliography

[1] ISO 5145, *Cylinder valve outlets for gases and gas mixtures — Selection and dimensioning*

[2] EN 1839, *Determination of explosion limits of gases and vapours*

[3] ASTM E 681, *Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases)*

[4] IEC/TR 60079-20, *Electrical apparatus for explosive gas atmospheres — Part 20: Data for flammable gases and vapours, relating to the use of electrical apparatus*

[5] IGC Document No. 139/07/E, *Safe Preparation of Compressed Oxidant Fuel Gas Mixtures in Cylinders*, Globally Harmonized Document, European Industrial Gases Association (EIGA), Brussels 2007

[6] SCHRÖDER, V., MACKRODT, B. and DIETLEN, S., *Determination of oxidizing ability of gases and gas mixtures*, ASTM STP 1395, Flammability and Sensitivity of Materials in Oxygen-Enriched Atmospheres: Ninth Volume (2000)

[7] SCHRÖDER, V., MOLNARNE, M., and MIZSEY, P., Flammability of gas mixtures: Part 1 and 2, *Journal of Hazardous Materials*, Volume 121, Issues 1-3, 20 May 2005, pp. 37-49

ICS 23.020.30; 71.100.20

Price based on 25 pages