



Calculation of Flammability and Lower Flammability Limits of Gas Mixtures for Classification Purposes

Volkmar Schroeder

Bundesanstalt für Materialforschung und -prüfung (BAM)
Division „Gases, Gas Plants“
Unter den Eichen 87
12205 Berlin

Berlin, 2016-09-09

Summary

ISO 10156:2010 contains a test method and a calculation method for flammability of gases and gas mixtures for the selection of cylinder valve outlets. The calculation method is used also to classify gas mixtures according to the national and international dangerous goods and dangerous substances regulations, e.g. according to the UN Recommendations on the Transport of Dangerous Goods (UN TDG) and the Globally Harmonized System of Classification and Labelling of Chemicals (UN GHS). The calculation method for gas mixtures requires substance parameters of the single components. These are the coefficients for the fire potential (T_{ci}) and for inerting ability, the so-called nitrogen equivalence (K_k), which have been estimated conservatively by means of flammability data.

BAM checked T_{ci} and K_k values of ISO 10156:1996 using three-component diagrams (Flammable gas-Inert-Air) of the CHEMSAFE® database. The experimental fundamentals and the principles of the calculation method are summarized in this paper. The revised data for T_{ci} and K_k values were adopted in the tables of ISO 10156:2010.

Furthermore, subcategorization of flammable gases has been proposed by a UN working group and shall be implemented in the GHS in the meantime. The subcategorization requires the lower flammability limit (LFL) as an additional indicator. Therefore, a test method and a calculation method for LFL were proposed by BAM and have been implemented in the new draft of ISO/CD 10156:2016.

The calculation method for gas mixtures is based on Le Chatelier's rule and was extended by using the K_k values for inert components in the mixture. The calculated LFLs of methane-inert gas mixtures were compared with experimental values for different types of inert gases. It could be shown that calculated LFLs are in good agreement with experimental values if the K_k values derived from three-component flammability diagrams are used. Although using the K_k values of ISO 10156:2010 leads to higher deviations, the results are still on the safe side.

Content:

	Page
Summary	2
1. Introduction	4
2. Flammability of Gases – Status Quo	4
2.1. UN Globally Harmonized System (UN GHS)	4
2.2. UN Recommendations on Transport of Dangerous Goods (UN TDG)	5
2.3. Standardized Test Procedures for Determination of Flammability Limits	5
3. Determination of Flammability according to ISO 10156	8
3.1. Test Procedure for Flammability	8
3.2. Calculation Method for Gas Mixtures	8
4. Determination of Lower Flammability Limits	11
4.1. Test Procedure for LFL	11
4.2. Proposed Calculation Method for Gas Mixtures	12
4.2.1. Mixtures of Flammable Gases and Mixtures of Flammable Gases with Nitrogen and/or Air	12
4.2.2. Mixtures of Flammable Gases with Air and Inert Gases other than Nitrogen	12
4.2.3. Examples	13
4.3. Comparison of Experimental and Calculated LFL	14
5. Conclusions	16
6. Literature	17

1 Introduction

One of the most important safety characteristics of gases and gas mixtures is their flammability in air. This information is necessary to prevent accidental fires and explosions during chemical processes, storage and transport. In many international regulations a gas or a gas mixture is classified as “flammable” if it has a flammability range in mixture with air under atmospheric conditions. For the determination of flammability the international Globally Harmonized System of Classification and Labelling of Chemicals (GHS) [1] refers to ISO 10156 [2], an international standard originally written for the determination of fire potential of gases and gas mixtures for the selection of cylinder valve outlets.

This standard contains a test method and a calculation method for the flammability of gases. The test method is based on ignition tests on flammable gas-air mixtures in a certain concentration range. The occurrence of a flame propagation from the spark electrodes through the ignition vessel is determined by visual observation.

The calculation method for gas mixtures needs substance indices, the so called „Tci values“ and “K_K values”, which characterize the fire potential of a flammable gas and the coefficient of nitrogen equivalency of an inert gas.

A new GHS working paper proposes to subcategorize the flammable gases of category 1 in “extremely flammable” and “flammable” gases. Following this proposal of a GHS Joint Working Group [3], the criterion for this sub-categorization is the lower flammability limit (LFL) or the fundamental burning velocity (FBV) of a gas or gas mixture. Furthermore, UN transport regulations [4] include a limitation for the flammability of gases at 13 mol% and a flammability range of not more than 12 percentage points. Therefore, the necessity of determining the flammability limits is given. It was proposed by ISO TC 58 working group to extend the standard ISO 10156 and supplement a test method and a calculation method for flammability limits. The calculation method should be used only for classification purposes, similarly as the calculation method for flammability (ignitability) for gas mixtures. Calculated values must be “on the safe side” but do not need to meet the true value exactly. In this end, a test method and a calculation method for flammability limits of gases and gas mixtures are included in the recent revision of ISO/CD 101256 [5].

The terms flammability limit (FL) and explosion limit (EL) have often the same meaning. In Europe the term “explosion limit” is frequently used as in the ATEX directives and in EN 13237:2012 [6]. In the US literature and in international standardization the wording “flammability limit” or “flammable limit” is more common.

2 Flammability of Gases - Status Quo

2.1 UN Globally Harmonized System (UN GHS)

In the GHS, a flammable gas is a gas having a flammable range with air at 20 °C and a standard pressure of 101.3 kPa and is subdivided in category 1 and 2.

Table 1: Gas categories according to GHS

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 percentages 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 when mixed with air

Note 1: Ammonia and methyl bromide may be regarded as special gases for some regulatory purposes

2.2 UN Recommendations on Transport of Dangerous Goods (UN TDG)

Flammable Gases are defined in the division 2.1 of the UN transport regulations as Gases, which at 20 °C and a standard pressure of 101,3 kPa:

- (i) are ignitable when in a mixture of 13 % or less by volume in air; or
- (ii) have a flammable range with air of at least 12 percentages points regardless of the lower flammable limit

2.3 Standardized Test Procedures for Determination of Flammability Limits

The “open vessel” and the “closed vessel” methods are the two, most frequently used test methods for the determination of explosion limits. In most cases the open vessel method uses vertical glass tubes (or flasks), in which a flame detachment and propagation is observed visually. The ignition vessel has a pressure relief to the atmosphere. ASTM E-681 [7], DIN 51649-1 [8] and EN 1839 (T) [9] are typical examples. The closed vessel method, e.g. ASTM E 918 [10], ASTM E 2079 [11] and EN 1839(B) [9] require pressure resistant autoclaves (bombs) as ignition vessels. The criterion is not the flame propagation, but a pressure rise after ignition. The US standard recommends a pressure rise of 7 % as threshold condition. The European standard is recommending a 5% criterion. In general, the flammability limits are affected by the material parameters, apparatus parameters and the applied criterion for an ignition. The most important are:

Material parameters:

1. Flammable mixture composition, type and amount of inert gas, fuel and oxidizer,
2. Initial temperature, initial pressure,
3. Flow state.

Apparatus parameters:

4. Determination procedure (step size, criterion for an ignition: pressure rise or flame propagation),
5. Type and size of the ignition vessel (closed, open, dimensions, material)
6. Ignition source (type, power, duration and location),
7. Direction of flame propagation.

BAM compared the European methods EN 1839 (T) and (B) with the German DIN 51649-1 and the US standard ASTM E 681. The German DIN 51649-1 test apparatus is also recommended by ISO 10156. The experimental parameters are summarized in Table 2.

All gas mixtures were prepared according to the partial pressures of the single components. For both tube methods (DIN 51649-1 and EN 1839 (T)) this was done in a separate 14-dm³ mixing vessel (explosion pressure resistant) at 2.0 bar (abs.). The ignition vessels were purged with about 12 dm³ of test mixture before firing the igniter. For the other two methods (ASTM E 681 and EN 1839 (B)) the components of test sample mixtures were filled directly into the ignition vessel and were homogenized by stirring before ignition.

Table 2: Apparatus parameters of the compared standard test methods for explosion limit determination at atmospheric pressure

	DIN 51649-1	EN 1839 (T)	EN 1839 (B)	ASTM E 681
Ignition vessel	glass cylinder, Ø = 60 mm, H = 300 mm	glass cylinder, Ø = 80 mm, H = 300 mm	closed spherical or cylindrical vessel V > 5 dm ³	glass flask, V = 5 dm ³
Ignition source	high voltage spark duration 0.5 s, power app. 10 W	high voltage spark duration 0.2 s, power app. 10 W	fused (exploding) wire, E = 10 J to 20 J or high voltage spark, duration 0.2 s	high voltage spark duration 0.5 s, power app. 10 W
Criterion	visually, flame detachment	visually, flame propagation of > 100 mm or halo of H > 240 mm	pressure rise ≥ 5% + pressure rise caused by the ignition in air	visually, flame spread as far as 13 mm from the wall (horizontal or vertical)
Number of repetition tests	5	4	4	1
Step size	0.1 mol% (FL ≤ 10 mol%), 0.2 mol% (FL > 10 mol%),	10 % rel., (FL ≤ 2 mol%), 0.2 mol% (FL > 2 mol%)	10 % rel., (FL ≤ 2 mol%), 0.2 mol% (FL > 2 mol%)	arbitrary, to be stated if more than 10% rel.
Explosion limit	last non-ignition point	last non-ignition point	last non-ignition point	Average value between last non- ignition point and first ignition point

For the ignition tests according to DIN 51649-1, EN 1839 (T) and ASTM E-681 a high voltage spark igniter was applied, as described in the standards. For the experiments according to EN 1839 (B) a spherical 14-dm³ stainless steel autoclave was used equipped with a fuse wire igniter in the center. The igniter was fired by means of special electronic equipment. This igniter consists of two insulated electrodes at a distance of 5 mm, holding a nickeline wire with a diameter of 0.12 mm at their ends. The ignition energy is provided by a 1.5 kVA/230 V insulating transformer, which is connected to the igniter by an electronic switching unit. The ignition energies were determined to be about 15 J for a burning time of 3.5 ms by measuring voltage and current. This type of igniter is recommended by EN 1839 (B) and by several EN and ASTM standards.

The selected concentration steps for the ASTM E 681 tests amounted to 0.2 mol% for all experiments. The results of the ignition tests are shown in Table 3. All reported limits are given as mole fractions in percent. For the test, 4 gases with different laminar burning velocities have been selected in the sequence from high to low: H₂, C₂H₄, CH₄ and NH₃.

Table 3: Explosion limits of hydrogen, ethylene, methane and ammonia in air [12]

	DIN 51649-1 (mol%)	EN 1839 (T) (mol%)	EN 1839 (B) (mol%)	ASTM E681 (mol%)
LFL (H₂ - Air)	3.8	3.6	4.2	3.75
UFL (H₂ - Air)	75.8	76.6	77.0	75.1
LFL (C₂H₄ - Air)	2.3	2.4	2.6	2.15
UFL (C₂H₄ - Air)	33.0	32.6	27.4	33.3
LFL (CH₄ - Air)	4.2	4.3	4.9	3.8
UFL (CH₄ - Air)	16.6	16.8	16.9	16.9
LFL (NH₃ - Air)	14.3	14.3	14.2	13.3
UFL (NH₃ - Air)	31.7	32.5	39.4	32.9

The observations can be summarized as follows:

- The procedures according to DIN 51649-1 and EN 1839 (T) produce identical results in nearly all cases. The reason is the very similar test apparatus of both methods.
- In many cases, the ASTM method leads to similar results as DIN 51649-1 and EN 1839(T). ASTM sometimes shows the widest explosion ranges. This can be explained by the use of a 5-dm³ flask in connection with the sensitive visual criterion.
- The closed vessel method EN 1839 (B) shows the highest deviations. LFLs measured by this method are higher compared to those from other methods. Also a clearly lower UFL was observed for ethylene. The reason might be that the pressure threshold criterion is less sensitive than the visual criterion.
- Ammonia is a special case of the considered gases showing a significant higher UFL in the closed vessel compared to the open vessel methods. Possibly the low laminar burning velocity combined with a large quenching distance of ammonia favoring ammonia reactions in the 14-dm³ sphere compared to smaller volumes contributes to this result. ASTM E 681 recommends in an annex for such substances applying a 12-dm³ sphere instead of 5 dm³.
- In general, the deviations between the results of the different methods obtained with gases, which are difficult to ignite, are higher. Typical examples is ammonia. Such reactions are more affected by apparatus parameters.

Britton [13] evaluated test methods for flammability limits in a survey paper in 2002. He also figured out, that closed vessel methods with a pressure rise criterion yield smaller flammability ranges compared to open vessel methods. Britton assumed that the preheated state of the gas mixture close to the spark in a glass tube is the reason for such wider ranges.

Recent investigations at BAM [14] using a windowed autoclave and applying both criteria at the same ignition test show, however, that flame propagation takes place already at pressure increases (p_{ex}/p_0) below 2 %.

Therefore, in order to avoid spread of flame, a flame propagation criterion should preferably be applied in explosion protection.

3 Determination of Flammability according to ISO 10156

3.1 Test Procedure for Flammability

ISO 10156 contains a test procedure for flammability according to the flame propagation criterion. 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. If a flame detachment combined with an upwards propagation of at least 100 mm is observed, the test substance is 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. If the chemical structure is unknown, the whole range of concentrations must be tested.

The test vessel is an upright glass cylinder having a minimum inner diameter of 50 mm and a minimum height of 300 mm (see Fig. 1). 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. A spark generator capable of supplying high voltage sparks (e.g. 15 kV, 30 mA, AC) with an energy of about 10 J is used. The spark gap is 5 mm and the spark duration 0.2 s to 0.5 s.

Test mixtures were prepared according to the partial pressures of the single components in closed pressure resistant mixing vessels at 2.0 bar(abs.).

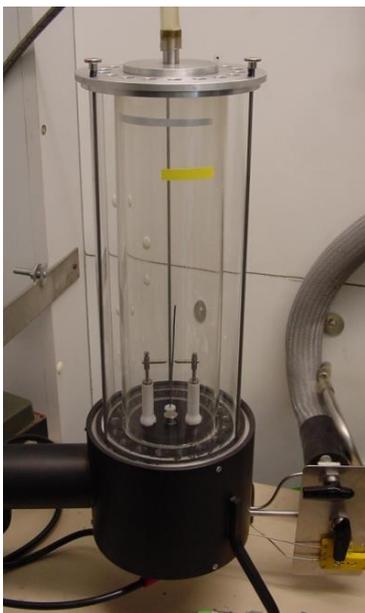


Fig. 1: BAM test apparatus acc. to ISO 10156

- open vessel
- glass tube (\varnothing 60 mm, minimum length 300 mm)
- high voltage spark igniter
- criterion: (upward) flame propagation > 100 mm

3.2 Calculation Method for Gas Mixtures

ISO 10156 proposes a method to calculate the flammability of gas mixtures using the so called Tci values. That method is recommended for gas mixtures produced in small quantities, e.g. special gases, if no experimental data are available. Furthermore, the calculation method takes into account not only the fire potential of the flammable component, but also the inerting capacity of the diluent gas in air.

A mixture can be classified as not flammable, if the following equation is satisfied:

$$\sum_{i=1}^n A_i \left(\frac{100}{T_{ci}} - 1 \right) \leq \sum_{k=1}^p B_k K_k \quad (1)$$

- A_i fraction of flammable component i in the mixture (mol%)
 n number of flammable components
 B_k fraction of inert component k in the mixture (mol%)
 p number of inert components
 K_k coefficient of nitrogen equivalency
 T_{ci} maximum flammable gas content for which a mixture of the flammable gas i in nitrogen is not flammable in air (mol%)

The T_{ci} for certain gas can be derived from flammability diagrams of the 3-component system flammable gas-inert gas-air (see Fig. 2).

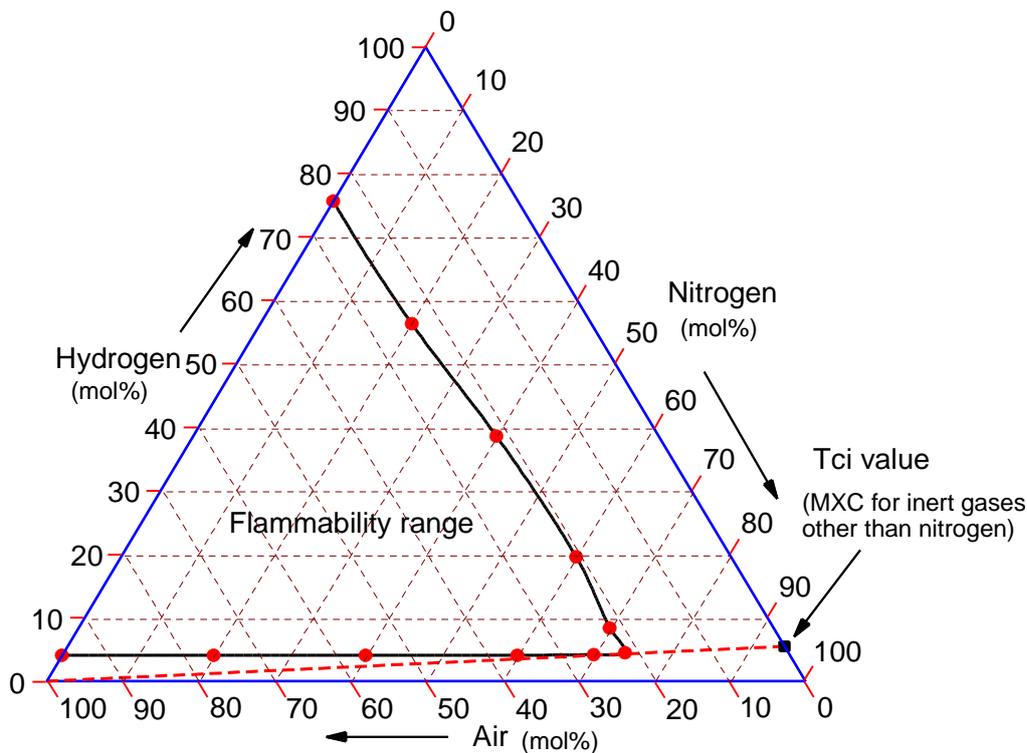


Fig. 2: Determination of T_{ci} (Example: Hydrogen)

The dashed red tangent represents a hydrogen-nitrogen mixture, which is mixed with any additions of air. The flammability range of hydrogen is not intersected. That means this hydrogen-nitrogen mixture does not form any explosive mixtures in dilution with air. The point of intersection of the tangent with the nitrogen axis is the so called T_{ci} value in accordance with the definition in ISO 10156. The hydrogen fraction of this point amounts to $T_{ci} = 5.5$ mol%. If such a gas mixture (5.5 mol% H_2 and 94.5 mol% nitrogen) would be tested according to the ISO 10156 test method, no flame propagation would be observed. This mixture is a non flammable gas.

For the determination of T_{ci} values the flammability ranges of ternary systems must be known as shown in Fig. 2. Therefore, it is necessary to measure the flammability limits (red points) of ternary gas mixtures, particularly the LFL at high nitrogen fractions. BAM measured a number of flammability ranges and published the ternary diagrams in a data book [15] and in the database CHEMSAFE® [16]. By help of these data T_{ci} and K_k values were calculated [17, 18].

Each inert gas has an ability to reduce the flammability range of flammable gas-air mixtures (see Fig. 3). The combustion reaction heats the inert gases to the temperature of the flame, which consumes a

part of the energy from the reaction. Some gases with inerting effects additionally affect the kinetics of the combustion or contribute partially to the combustion. Brominated and chlorinated hydrocarbons often show such inhibiting effects, while partially halogenated hydrocarbons with hydrogen atoms in the molecule contribute frequently to combustion. These gases are not really inert and not suitable for the calculation method.

The ability to reduce the flammability range is expressed by the dimensionless K value, the so-called coefficient of nitrogen equivalency. In Fig. 3 the flammability ranges of methane with different inert gases are shown. Additionally the MXC values (T_{ci} in case of nitrogen) are listed in the box. It can be seen clearly that the explosion ranges are strongly influenced by different inert gases. The explosion ranges of methane are much more reduced by inert gases with high molar heat capacity than by gases having low heat capacities. The MXC values rise with increasing heat capacities. Furthermore, other physical gas parameters affect the inerting ability, such as the thermal conductivity and the diffusion coefficient.

If the inert gas partially reacts, the LFL drops down. Therefore, MXC does no longer correspond to the heat capacity of inert gas (red marked in Fig. 3 for R134a).

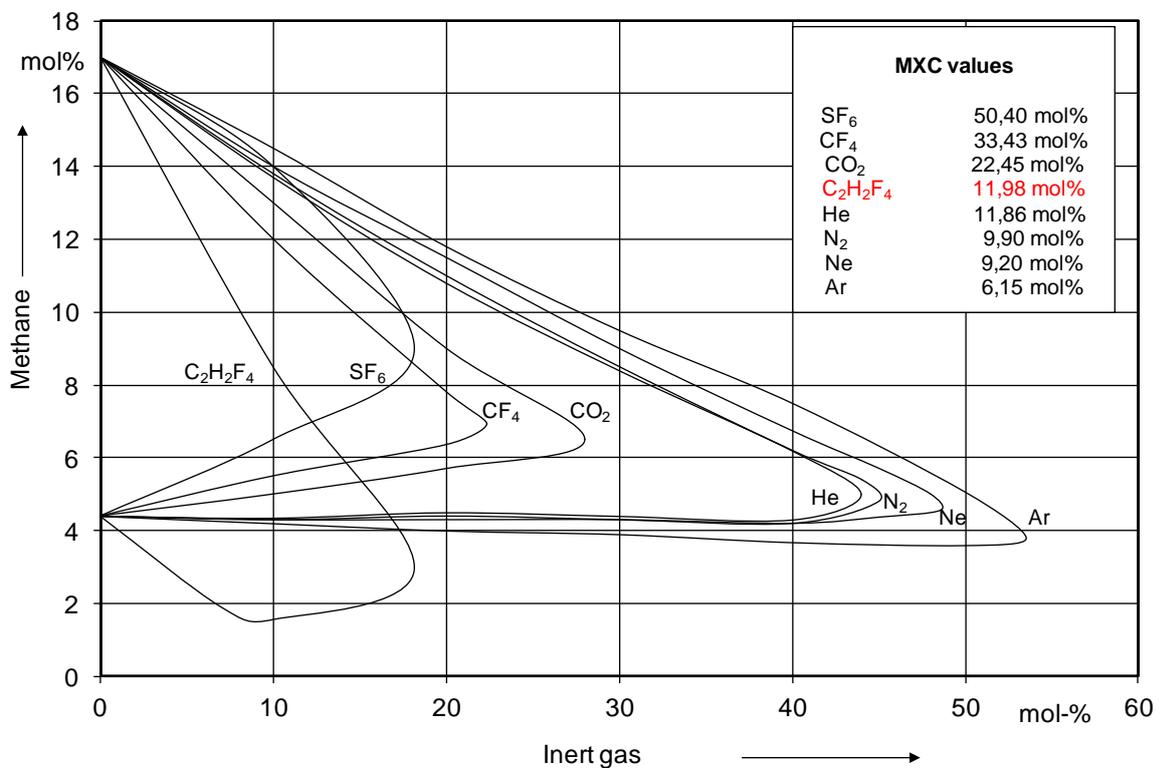


Fig. 3: Flammability ranges of methane in air with different inert gases [16]

The calculation of coefficients of nitrogen equivalency of the k -th inert gas component relative to nitrogen can be carried out for each flammable-inert gas system. In this way one can get several, flammable gas specific coefficients ($K_{i,k}$) from experimental data ($MXC_{i,k}$ and T_{ci}) using the reformulated Eq. (1). At the limiting value for flammability of a mixture, composed of only one inert gas k and one flammable gas i , it resolves to:

$$K_{i,k} = \frac{MXC_{i,k} * \left(\frac{100}{T_{ci}} - 1 \right)}{(100 - MXC_{i,k})}, \quad (2)$$

- i is the index of the flammable gas,
- k is the index of the inert gas other than nitrogen and

MXC is the maximum flammable gas content for which a mixture of the flammable gas i in an inert gas other than nitrogen is not flammable in air in mol%).

Experimental flammable gas specific coefficients ($K_{i,k}$) show minor deviations depending on the flammable gas, whilst the inert gas has the most significant influence.

T_{ci} values and K values of gases are listed in ISO 10156:2010. If no exact experimental values were available, they were estimated conservatively. In case of T_{ci} the LFL were taken and in case of K molar heat capacities and molecular structure were considered.

Equation 1 can be used in all cases where Le Chatelier's rule [19] is valid in good approximation. It is based on the assumption that single heats of combustion of the components can be summed up and a certain constant flame temperature must be reached in the mixture. This is frequently the case for LFL and T_{ci} of flammable gases and "diluted" flammable gases in mixture with inert gases. The rule fails if the combustion kinetics is influenced, e.g. by inhibitors.

4 Determination of Flammability Limits

4.1 Proposed Test Method for Flammability Limits of Gases

The revised version of ISO/CD 10156 [6] has been supplemented by a test method for flammability limits in addition to the existing method for flammability of gases. The test apparatus is the same as applied for the flammability determination. Unlike for the determination of flammability in general, it is necessary to apply a different test procedure for determining flammability limits (FL).

As shown in chapter 2.3, an open vessel method with a flame-propagation criterion fulfills most of the requirements of national standards.

Apparatus and test method are very similar to DIN 61649-1 (see Table 2). The characterization of flammability limits consists of determining the amount of test substance in air at 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 mol% for FL below 10 mol% and 0.2 mol% for FL equal or above 10 mol%. Prior to each ignition attempt, the test vessel is purged with the test mixture. The purging volume has to be at least ten times the volume of the test vessel. An ignition is attempted using the induction spark under quiescent conditions. It is observed whether a flame detaches from the ignition source and propagates at least 100 mm upwards. 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) has to be confirmed with four additional tests. The determination is concluded when no flame detachment is observed in all five tests. If flame detachment does occur, the test gas content has to be changed further by reducing (lower flammability limit) or increasing (upper flammability limit) the test gas content by one increment. The flammability limit is the test gas concentration in mixture with air at which an ignition just fails.

4.2 Proposed Calculation Method for LFL of Gas Mixtures

As mentioned in chapter 3.2 for mixtures of flammable gases Le Chatelier's formula is commonly used to predict lower flammability limits (LFL). Le Chatelier's formula cannot be used for calculation of upper flammability limits. Furthermore, it cannot be used for partial halogenated hydrocarbons or oxidizers other than air. The formula can be applied for mixtures being flammable but not for mixtures being potentially explosive.

According to this formula the lower flammability limit of a mixture of fuel gases (LFL_M) is given according to the following equation (Le Chatelier's rule):

$$\frac{100}{LFL_M} = \frac{A_1}{LFL_1} + \frac{A_2}{LFL_2} + \dots + \frac{A_n}{LFL_n} \quad (3)$$

LFL Lower flammability limit in mol%
A Molar fraction in mol% of the single flammable gas

For classification purposes this formula can also be used for mixtures of “diluted” flammable gases that means fuel gas-inert gas mixtures.

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

Equation (4) can be used in good approximation for mixtures of flammable gases, nitrogen and air:

$$LFL_M = \frac{100}{\sum_i^n \frac{A_i}{LFL_i}} \quad (4)$$

4.2.2 Mixtures of Flammable Gases with Air and Inert Gases other than Nitrogen

The following formula takes into account the nitrogen equivalency (K_k) of inert gases other than nitrogen. The change in molar heat capacity of the air-inert mixture at LFL_M influences the necessary fuel concentration (heat of combustion) for flame propagation. LFL_M is conservatively estimated because of the safety margin that is included in K_k values given by ISO 10156.

$$LFL_M = \frac{100}{\sum_i^n \frac{A_i}{LFL'_i}} \quad (5)$$

Where LFL'_i is given by good approximation:

$$LFL'_i = \frac{(100 - LFL'_M - (1 - \bar{K}) \frac{\sum_{p=1}^k B_k}{\sum_{i=1}^n A_i} * LFL'_M)}{(100 - LFL'_M)} * LFL_i \quad (6)$$

LFL'_M Lower flammability limit of the mixture of only flammable gases, calculated according to Eq. (4)

\bar{K} Average of K_k values of the inert gases weighted according to its molar fractions

A_i Molar fraction of flammable gas i in mol%, based on the mixture of which LFL_M is to be calculated

B_k Molar fraction of inert gas k in mol%, based on the mixture of which LFL_M is to be calculated

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

4.2.3 Examples

In the following some examples are given to illustrate the the calculation of LFL.

Example 1

Consider a mixture of two flammable gases, 80% methane and 20 % ethane. Using Eq. (4) with $LFL_{(CH_4)} = 4,4$ mol% and $LFL_{(C_2H_6)} = 2,4$ mol% the lower flammability limit of mixture is:

$$LFL_M = \frac{100}{\sum_{i=1}^n \frac{A_i}{LFL_i}} = \frac{100}{\frac{80}{4,4} + \frac{20}{2,4}} = 3,8 \text{ mol\%}$$

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. Using Eq. (4) with $LFL_{(H_2)} = 4,0$ % the lower flammability of mixture is:

$$LFL_M = \frac{100}{\sum_{i=1}^n \frac{A_i}{LFL_i}} = \frac{100}{\frac{48}{4,0}} = 8,3 \text{ mol\%}$$

Example 3

Consider a mixture of 40% methane and 60% carbon dioxide. The mixture is flammable and not potentially explosive. Using Eq. (5), $LFL'_M = LFL_{(CH_4)} = 4,4$ % and $K_{(CO_2)} = \bar{K} = 1,5$ the lower flammability of mixture is:

$$LFL'_i = \frac{\left(100 - LFL'_M - (1 - \bar{K}) \frac{\sum_{p=1}^k B_k}{\sum_{i=1}^n A_i} * LFL'_M\right)}{(100 - LFL'_M)} * LFL_i = \frac{(100 - 4,4 + 0,5 * \frac{60}{40} * 4,4)}{100 - 4,4} * 4,4 =$$

$$= 4,55 \text{ mol\%}$$

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

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. Using Eq. (5) with $LFL_{(H_2)} = 4,0$ %, $LFL_{(CH_4)} = 4,4$ %, $K_{(CO_2)} = 1,5$, $K_{(N_2)} = 1,0$ and $K_{(air)} = 1,0$ the lower flammability of the mixture is:

$$LFL'_M = \frac{100}{\sum_{i=1}^n \frac{A_i}{LFL_i}} = \frac{100}{\frac{50}{4,4} + \frac{50}{4,0}} = 4,2 \text{ mol\%}$$

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

$$LFL'_{CH_4} = \frac{\left(100 - LFL'_M - (1 - \bar{K}) \frac{\sum_{p=1}^k B_k}{\sum_{i=1}^n A_i} * LFL'_M\right)}{(100 - LFL'_M)} * LFL_i = \frac{(100 - 4,2 + 0,21 * \frac{70}{30} * 4,2)}{100 - 4,2} * 4,4 =$$

$$= 4,5 \text{ mol\%}$$

$$LFL'_{H_2} = \frac{(100 - 4,2 + 0,21 * \frac{70}{30} * 4,2)}{100 - 4,2} * 4,0 = 4,1 \text{ mol\%}$$

$$LFL_M = \frac{100}{\sum_{i=1}^n \frac{A_i}{LFL_i}} = \frac{100}{\frac{15}{4,5} + \frac{15}{4,1}} = 14,3 \text{ mol}\%$$

5 Comparison of Experimental and Calculated LFL

For validation of Eq. (4) and (5) experimental LFL were compared with calculated ones. The experimental lower flammability limits of methane and methane-inert gas mixtures were compared with calculated values using the Kk coefficients of ISO 10156:2010. As Kk coefficients for classification purposes are estimated conservatively, calculated LFL should be lower than experimental ones to be on the “safe side”. In Figure 4 the experimental LFL of methane in mixture with the inert gases argon, nitrogen, carbon dioxide and tetrafluoromethane are shown. The inert gases have increasing molar heat capacities and increasing inerting abilities. Figure 5 shows the calculated values using the ISO Kk.

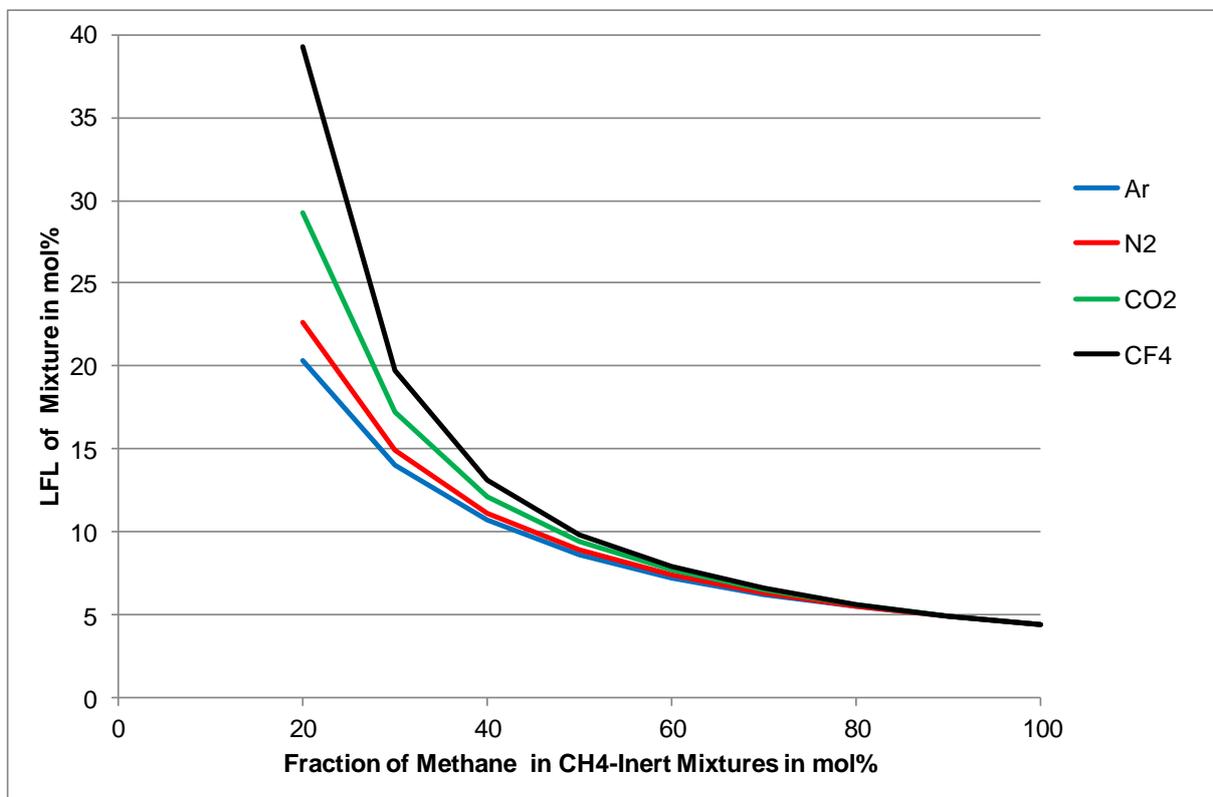


Fig. 4: Experimental LFL of Methane-Inert mixtures

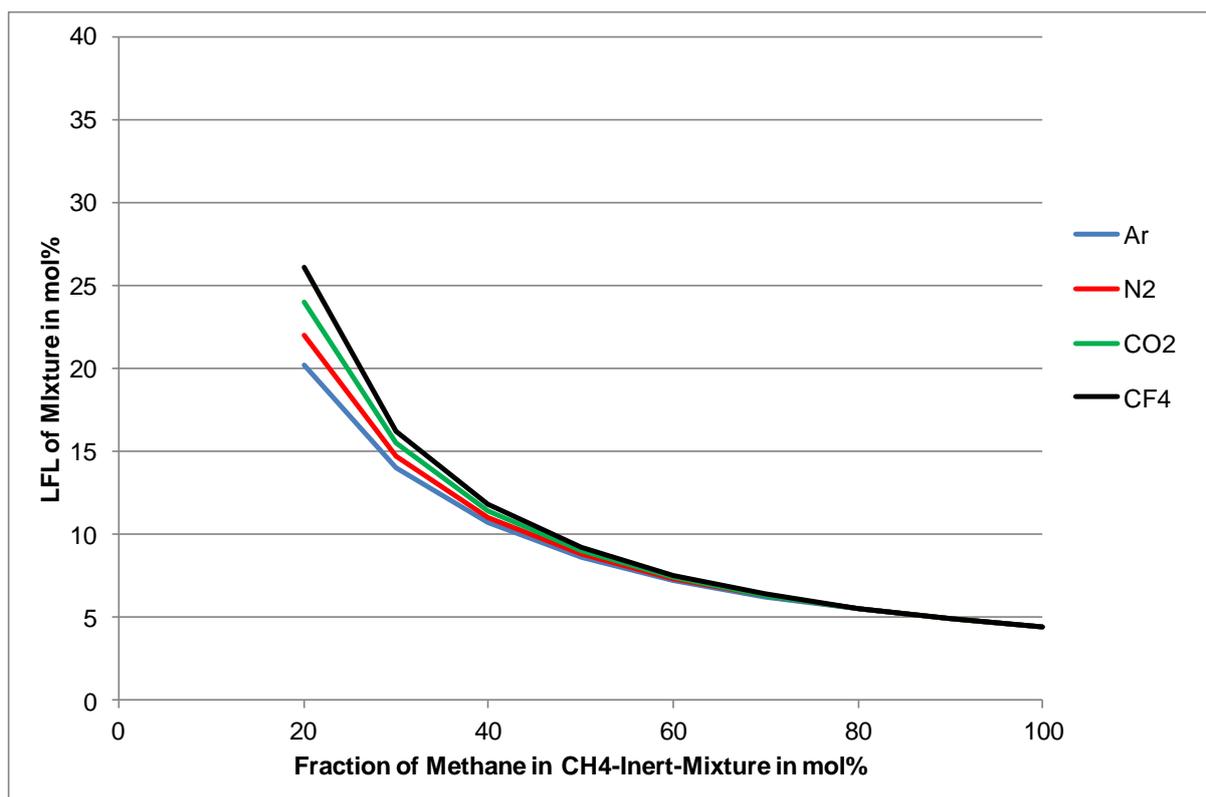


Fig. 5: Calculated LFL of Methane-Inert mixtures using Kk values from ISO 10156

Heat capacities and Kk values are given in Table 4. Kk(experimental) was calculated according to Eq. (2) using the experimental MXC from Fig. 3 for the fuel gas methane.

Table 4: Molar heat capacities and Kk values for selected inert gases

Inert Gas	Cp in J mol ⁻¹ K ⁻¹ at 700 K [20]	Kk (experimental) (fuel gas: Methane)	Kk ISO 10156
Argon	20,8	0,60	0,55
Nitrogen	30,7	1,00	1,00
Carbon dioxide	49,6	2,63	1,50
Tetrafluoromethane	91,6	4,57	2,00

Particularly in case of higher amounts of inert gases the calculated LFL for gas mixtures are too small compared to experimental values (see Fig. 5 vs. Fig. 4). That is because conservative ISO Kk are used for the calculation method. Calculated and experimental LFL for the flammable gas-inert mixtures are nearly identically, when experimental Kk are used. Fig. 6 shows an example for carbon dioxide.

Nevertheless, for classification purposes, the LFL calculated with ISO Kk can be used. Although having lower values, these are still conservative.

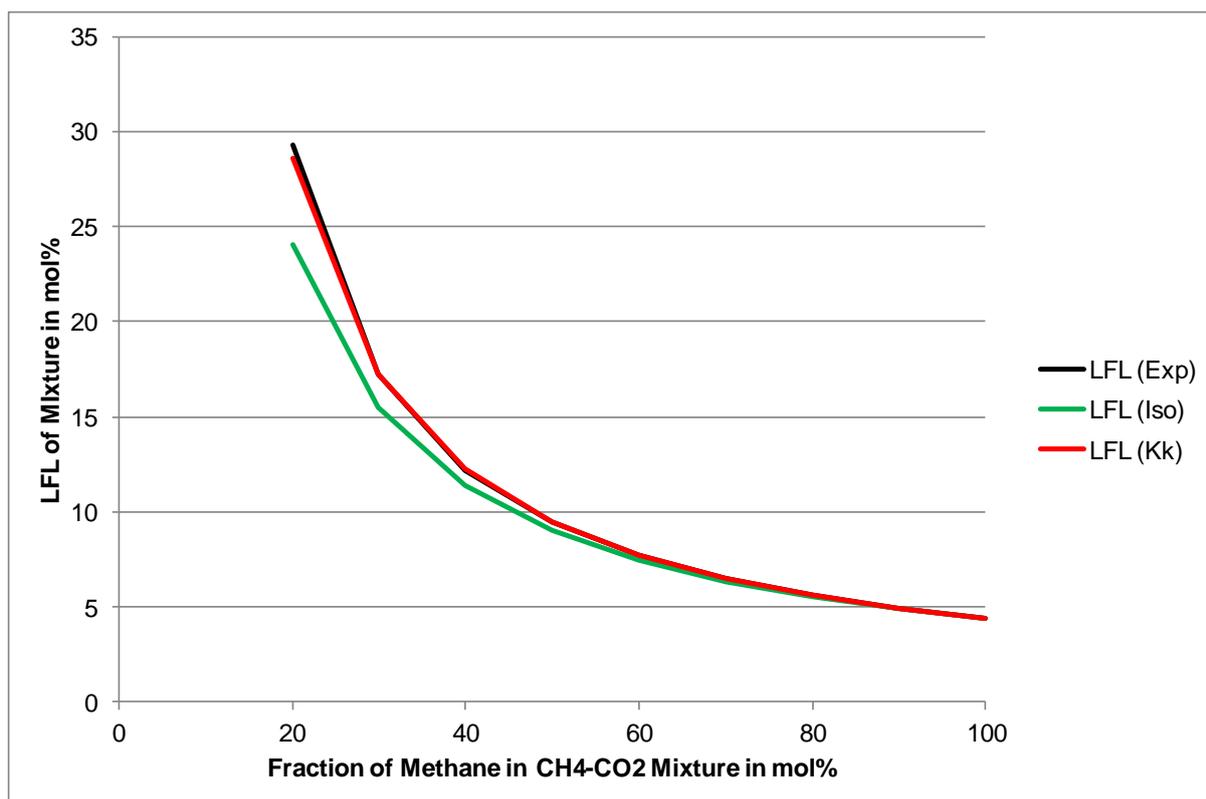


Fig. 6: Calculated LFL of Methane-CO2 mixtures using Kk values from ISO 10156 and Kk derived from ternary diagrams

6 Conclusions

BAM evaluated older Tci and KK values from ISO 10156:1996 using three-component diagrams (Flammable gas-Inert-Air) from the CHEMSAFE® database. The experimental fundamentals and the principles of calculation methods for the determination of Tci and Kk values are summarized in this paper. It could be shown, that some old Tci and Kk must be corrected. It must be mentioned that the calculation of flammability of gas mixtures according to Eq. (1) is only possible if real inert gases are present in the mixture. Non-flammable gases that partially burn or influence the kinetics of combustion reaction, can lead to errors in the calculation method (see Fig. 3, C₂H₂F₄). The revised data for Tci and Kk values were adopted in the tables of ISO 10156:2010. Because of the weak dependency of Kk values on the type of flammable gas, Kk was estimated conservatively in ISO 10156:2010 for safety reasons.

Furthermore, subcategorization of flammable gases has been proposed by a UN working group and should be implemented in the GHS in the meantime. The subcategorization requires the lower flammability limit (LFL) as an additional indicator. Therefore, a test method and a calculation method for LFL were proposed by BAM and have been implemented in the new draft of ISO/CD 10156:2016.

The proposed calculation method for gas mixtures is based on Le Chatelier's rule and was extended by using the Kk values for inert components in the mixture. The calculated LFLs of methane-inert gas mixtures were compared with experimental values for different types of inert gases. It could be shown that the calculated LFLs are in a very good agreement with experimental LFLs, if Kk values which have been derived from three-component flammability diagrams are used. If using the Kk values from ISO 10156:2010, the deviations to experimental LFL are higher, but always on the safe side.

7 Literature

- [1] Globally Harmonized System of Classification and Labelling of Chemicals (UN GHS), <http://www.unece.org/trans/danger/danger.html>
- [2] ISO 10156:2010, Gases and gas mixtures -- Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets,
- [3] UN working paper ST/SG/AC.10/C.4/2016/4 - ST/SG/AC.10/C.3/2016/17, <http://www.unece.org/fileadmin/DAM/trans/doc/2016/dgac10c4/ST-SG-AC.10-C.4-2016-4e-ST-SG-AC.10-C.3-2016-17e.pdf>
- [4] UN TDG, UN Recommendations on the Transport of Dangerous Goods - Model Regulations, Nineteenth revised edition <http://www.unece.org/trans/danger/danger.html>
- [5] ISO/CD 101256:2016, Gases and gas mixtures -- Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets
- [6] EN 13237:2012, Potentially explosive atmospheres. Terms and definitions for equipment and protective systems intended for use in potentially explosive atmospheres,
- [7] ASTM E681, Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases)
- [8] DIN 51649-1, Bestimmung der Explosionsgrenzen von Gasen und Gasgemischen in Luft
- [9] EN 1839, Determination of explosion limits of gases and vapours
- [10] ASTM E 918, Standard Practice for Determining Limits of Flammability of Chemicals at Elevated Temperature and Pressure
- [11] ASTM E 2079, Standard Test Methods for Limiting Oxygen (Oxidant) Concentration in Gases and Vapors
- [12] Schroeder, V., Daubitz, R., Evaluation of standard test methods for the determination of explosion limits of gases and vapors, in: Proceedings of the 11th International Symposium of Loss Prevention, Praha, Czech Republic, 2004, pp. 2109–2117
- [13] L.G. Britton, Two hundred years of flammable limits, *Process Saf. Prog.* 21 (1) (2002) 1–11
- [14] Tschirschwitz, R., Schroeder, V., Brandes, E. and Krause, U., Determination of explosion limits - criterion for ignition under non-atmospheric conditions, Proceedings of 10th International symposium on hazards, prevention, and mitigation of industrial explosions - X ISHPMIE (2014)
- [15] Molnarne, M., Schendler, Th., Schroeder, V., Safety characteristic data, volume 2: Explosion regions of gas mixtures, NW-Verlag, Bremerhaven, 2008
- [16] CHEMSAFE®, Database of evaluated safety characteristics, DECHEMA, BAM und PTB, Frankfurt/M., Germany, Update 2014
- [17] Schroeder, V. and Molnarne, M., *Journal of Hazardous Materials A121* (2005) 37–44
- [18] Molnarne M., Mizsey, P. and Schroeder, V., *Journal of Hazardous Materials A121* (2005) 45–49
- [19] Le Chatelier, H. L., Note sur le dosage du grisou par les limites de inflammabilité, *Annales des mines* 19 (1891) 388–395
- [20] B. E. Poling, J. M. Prausnitz and J. P. O'Connell: "The Properties of Gases and Liquids", McGraw-Hill, New York 2001