

Flammability of gas mixtures Part 2: Influence of inert gases

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Abstract

Ternary systems, which contain flammable gas, inert gas and air, were studied in order to give the user an evaluation of the ISO 10156 calculation method for the flammability of gas mixtures. While in Part 1 of this article the fire potential of flammable gases was the focal point, the influence of inert gases on the flammability of gas mixtures was studied in Part 2. The inerting capacity of an inert gas is expressed by the dimensionless K value, the so-called “coefficient of nitrogen equivalency”. The experimental determination of K values is demonstrated by using explosion diagrams. The objective of this study was to compare the estimated results, given by ISO 10156, with measurements of explosion ranges based on the German standard DIN 51649-1, given by CERN and CHEMSAFE. The comparison shows that ISO 10156, Table 1, supplies conservative K values, which can be regarded as safe in all cases. Nevertheless, in a number of cases ISO underestimates the inerting capacity, so that non-flammable gas mixtures are considered flammable.

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1. Introduction

The calculation method published in ISO 10156 [1], Chapter 4.6 takes into account not only the fire potential of the flammable component, but also the inerting capacity of the diluent gas in air.

Each inert gas has an ability to reduce the flammable range of flammable gas–air mixtures. The combustion reaction heats the inert gases to a certain flame temperature, which consumes a part of the energy from the reaction. Some “inert gases” additionally affect the kinetics of the combustion. Halogenated hydrocarbons often show such inhibiting effect. The ability to reduce the flammable range is expressed by the dimensionless K value, the so-called coefficient of nitrogen equivalency.

The calculation method is based on the fulfilment of the following criterion:

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

where A_i is the fraction of flammable component i in the flammable gas–inert gas mixture, in percent by volume (or mol%), n the number of flammable components, B_k the fraction of inert component k in the flammable gas–inert gas mixture, in percent by volume (or mol%), p the number of inert components, K_k the coefficient of nitrogen equivalency and T_{ci} is the maximum flammable gas content for which a mixture of the flammable gas i in nitrogen is not flammable in air, in percent by volume (or mol%). Remark: in the following it will be written as T_{ci} in accordance with Part 1 [2].

Gas mixtures, for which this condition is not fulfilled, have to be classified as flammable.

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In Part 1 of this article [2], the fire potential of the flammable components (left-hand side of Eq. (1)) has been discussed; therefore, Part 2 deals with inerting capacities of the inert components (right-hand side of Eq. (1)). The determination of K_L values is demonstrated by means of explosion diagrams.

2. Explosion diagrams of hydrocarbons with different inert gases

Besnard's report provides an excellent example for the influence of inert gas on explosion ranges [3]. He investigated systematically a number of ternary systems in order to find non-flammable mixtures, which are needed as "magic gases" in indication chambers of particle accelerators in the European Centre for Nuclear Research (CERN). Besnard used an apparatus based on DIN 51649-1. This apparatus was developed and manufactured in cooperation with BAM twice, first for the tests in Berlin and another time for CERN in Geneva. It complied with the testing equipment described in ISO 10156, Fig. 1. The apparatus and the test procedure are described in detail in Part 1 of this article [2].

Besnard's experimental results are summarized in Figs. 1–4 [3] with the flammable gases methane, ethane, propane and *n*-butane and a number of inert gases.

In addition to the influence of the specific heat, partially halogenated hydrocarbons show another effect. The lower explosion limits of flammable gases in Figs. 1–4 decrease strongly on addition of $C_2H_2F_4$ (R134a) and exhibit anomalous courses. The reason is that a number of partially halogenated hydrocarbons take part in the combustion reaction without themselves being flammable as pure materials in air. Such substances are not really "inert" and can often ignite in air under high pressure or temperature, as described in Part 1 of this article. If one determines the so-called MXC values from those explosion diagrams, very low values will be obtained, even if their specific heat values are high.

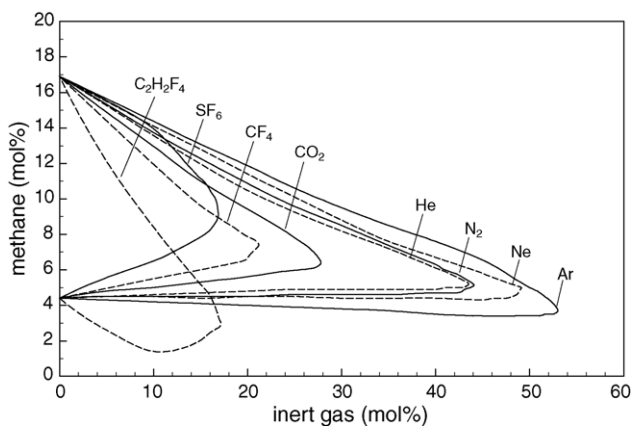


Fig. 1. Influence of inert gas on the explosion ranges of methane–inert gas–air mixtures, measured according to DIN 51649-1 at 20 °C and 101 kPa [3].

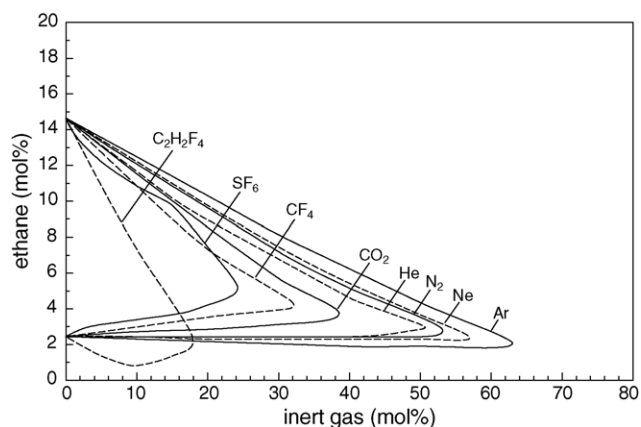


Fig. 2. Influence of inert gas on the explosion ranges of ethane–inert gas–air mixtures, measured according to DIN 51649-1 at 20 °C and 101 kPa [3].

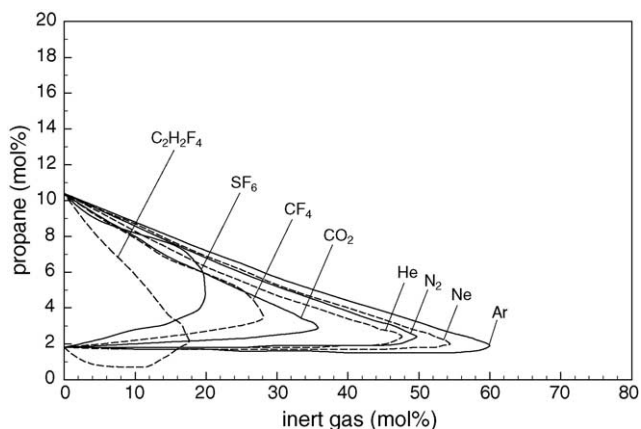


Fig. 3. Influence of inert gas on the explosion ranges of propane–inert gas–air mixtures, measured as per DIN 51649-1 at 20 °C and 101 kPa [3].

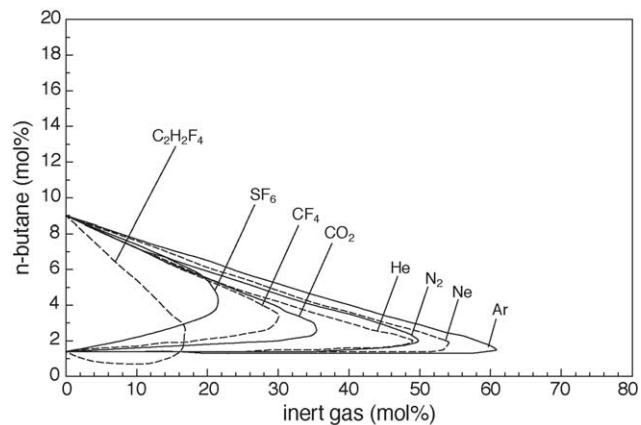


Fig. 4. Influence of inert gas on the explosion ranges of *n*-butane–inert gas–air mixtures, measured according to DIN 51649-1 at 20 °C and 101 kPa [3].

3. K values calculated from experimental data

The measurements of [3–5] allow the accuracy test of the coefficients of nitrogen equivalency K_k for inert gases recommended by ISO 10156. Therefore, one has to draw the tangent from the point “100% air” to the explosion range (see Fig. 5) and determine the MXC value for the inert gas to be evaluated. The MXC value is defined – similarly to the T_{ci} value, which is valid only for nitrogen as an inert gas – as the maximum flammable gas content for which the mixture of the flammable gas i with the inert gas k is not flammable in air.

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 ignitability of a mixture, composed of only one inert gas k and one flammable gas i , it becomes:

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

where i is the index of the flammable gas, k 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 percent by volume (or mol%).

The K_k values were calculated from CHEMSAFE data (see Table 1) and also from Besnard’s measurements (see Table 2). The experimental MXC values were derived from the explosion diagrams, the T_{ci} values were taken from Part 1, Table 5.

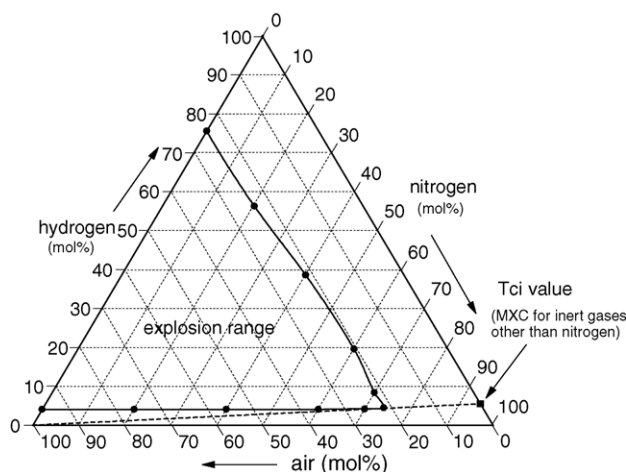


Fig. 5. Explosion diagram of the hydrogen–nitrogen–air system, measured at 20 °C and 101 kPa according to DIN 51649-1.

Table 1

K_k values determined from [3] at 20 °C and 101 kPa

Gases	Ar	Ne	He	N ₂	CO ₂	CF ₄	SF ₆	R134a
Methane	0.62	0.93	1.20	1.00	2.27	3.37	5.09	1.21
Ethane	0.62	0.88	1.10	1.00	1.84	2.63	4.13	1.45
Propane	0.65	0.81	1.04	1.00	1.87	2.77	4.80	1.58
Isobutane	0.59	0.80	1.01	1.00	1.94	2.32	4.74	1.40
<i>n</i> -Butane	0.64	0.77	1.01	1.00	1.84	2.61	4.78	1.63
“Average”	0.62	0.84	1.07	1.00	1.95	2.74	4.71	1.45
“Worst case”	0.59	0.77	1.01	1.00	1.84	2.32	4.13	1.21

Table 2

K_k values determined from [4,5]

Gases	CO ₂ (20 °C)	H ₂ O ^a (100–110 °C)	Ar (20 °C)	He (20 °C)	R134a (20 °C)
Methane	2.23	1.87	0.69	1.31	–
Ethane	1.87	1.40	–	–	–
Propane	1.93	1.51	–	–	1.81
Ethylene	1.84	1.68	–	–	–
Propylene	1.92	1.36	–	–	–
Hydrogen	1.51	1.35	0.75	1.62	–
CO + 1% H ₂	1.86	–	–	–	–
CO (wet N ₂)	1.77	1.30	0.56	0.92	–
“Average”	1.87	1.50	0.67	1.28	1.81
“Worst case”	1.51	1.30	0.56	0.92	1.81

^a The comparison includes the temperature dependence of T_{ci} . Note that in most cases the legal classification of gas mixtures corresponds to atmospheric conditions.

4. Evaluation of K values recommended by ISO 10156

Table 3 summarizes the K_k values from [3–5] which are taken from the rows “average” and “worst case” of Tables 1 and 2. Furthermore, the K_k range for each inert gas with the lowest and highest values from Tables 1 and 2, achieved by using different flammable gases, are given. Shebeko et al. [6], using enthalpy calculations, have also found the K value for SF₆ with isobutane to be around 4.

The average K_k values show that the ISO 10156 recommendations are in most cases on the “safe” side. An exception is water vapour, because here, in addition, influence of temperature has to be taken into account. However, the K values cannot be considered mechanically (taken simply the mathematical average values) since, for safety purposes, the “worst case” must be selected for design or decision.

If the intervals of the individual K_k values are considered, it can be stated that the recommendations of ISO 10156 for helium, SF₆ and CF₄ are too conservative.

5. Discussion

The comparison shows that the estimated ISO values are in good agreement with experimental values. Apart from some exceptions the specific heat of inert gases plays the most im-

Table 3

Comparison of the K_k values from Tables 1 and 2 with the K_k values published in the ISO 10156 standard

	CO ₂	He	Ar	Ne	Kr	Xe	SO ₂	SF ₆	CF ₄	R134a	H ₂ O (100–110 °C)
K_k from ISO	1.5	0.5	0.5	0.5	0.5	0.5	1.5	1.5	1.5	–	1.5
K_k average [3]	1.95	1.07	0.62	0.84	–	–	–	4.71	2.74	1.45	–
K_k average [4,5]	1.87	–	0.67	–	–	–	–	–	–	1.81	1.50
Minimum K_k^a [3–5]	1.51	0.92	0.56	0.77	–	–	–	4.13	2.32	1.21	1.30
Maximum K_k [3–5]	2.27	1.31	0.75	0.93	–	–	–	5.09	3.37	1.81	1.87

^a The minimum K_k values [3–5] represents the “worst case”.

portant role for the inerting capacity. Because of the influence of apparatus parameters on the determination of explosion limits it is strongly recommended to determine K values only by using explosion diagrams, which are measured using the same test procedure.

The database CHEMSAFE [5] supplies explosion diagrams, which are measured according to the DIN 51659-1 in most cases, recommended by experts of the BAM and the Physikalisch-Technische Bundesanstalt (PTB). Besnard has determined a number of explosion diagrams for hydrocarbons with eight different inert gases: nitrogen, argon, neon, helium, CO₂, CF₄, SF₆ and R134a [3]. He used a similar test apparatus like the one of BAM based on DIN 51649-1.

Using the measurements, a rank can be determined for the inerting capacity of inert gases. This inerting capacity is defined with reference to the flammability of a flammable gas–inert gas mixture in air. It does not correspond to the total reduction of the explosion range in an explosion diagram. Therefore, it can be recommended to apply the K values for classification purposes to determine the flammability of gas mixtures in air, but the K value should not be used to estimate the potential explosion hazard of gas mixtures close to the upper explosion limit.

The rank of the inerting ability is SF₆ > CF₄ > CO₂ > R134a > H₂O > He > N₂ > Ne > Ar. This corresponds to the rank of the specific heat values of the inert gases (see Fig. 6). A higher specific heat value means better inerting effect. C_p values at 700 K were used for this simple comparison, taken into account the range of heating up from room temperature to flame temperature at the lower explosion limits.

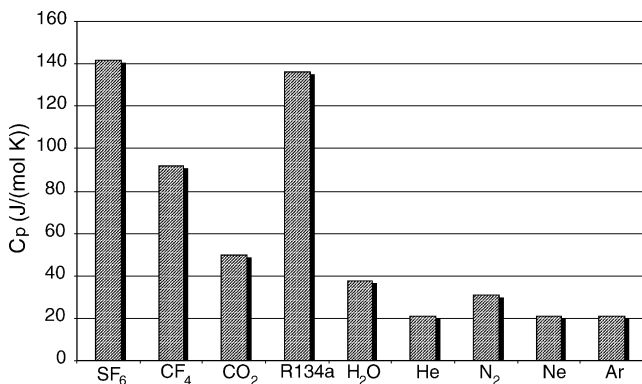


Fig. 6. Specific heats of inert gases calculated at 700 K based on [7] and in the case of R134a based on [8].

However, three important anomalies can be observed:

- helium shows better inerting effect than it would be expected from its specific heat;
- in the case of the hydrogen the inerting effect of CO₂ is worse than expected;
- R134a shows a worse inerting effect than it would be expected from its position in the specific heat rank.

The better inerting effect of helium than expected from its specific heat may be due to its extremely good thermal conductivity. In the case of hydrogen, the worse inerting effect of carbon dioxide can be explained by the fact that carbon dioxide does not really behave as an inert substance with hydrogen. A possible reaction between the two components is the backward water gas shift reaction, which can take place at flame temperature. The anomalous behaviour of partially halogenated hydrocarbons such as R134a is already discussed above.

These phenomena show that the evaluation of the flammable–inert gas mixtures is a complex issue and careful investigations are needed to determine whether or not the evaluated mixture is in the dangerous explosive zone.

6. Conclusions

A comparison of the T_{ci} values (see Part 1 of this article) indicates that the constants in the calculation method for flammability of gas mixtures in the ISO 10156 (1996) standard need to be revised. These constants are based on old measurements from the literature without giving the literature sources, and differ significantly from latest measured data according to German standard DIN 51649-1 or data taken from new European and US standards. Use of the ISO data for the calculation of flammability of gas mixtures can result in wrong classification and finally in explosion hazard.

On the other hand, it should be noted that the “worst case” K values, which are determined from experiments, do not differ significantly from the proposed estimated values of ISO 10156 (1996) for all investigated inert gases.

Acknowledgement

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