

Safety characteristics at non-atmospheric conditions - oxidizers other than air

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Abstract

Nitrous oxide is used as an oxidizer in the chemical industry. It is an oxidizer with enhanced oxidizing potential compared to air, but its handling is not as critical as the handling of pure oxygen. Safety characteristics with N₂O as an oxidizer differ remarkably from those in air which are mostly well known. Experimental values of lower explosion limits LEL_{N₂O}, limiting oxidizer fractions LOF_{N₂O} and maximum experimental safe gaps MESG_{N₂O} for fuels in a mixture with N₂O are reported and compared to those of flammable substance/air mixtures. Based on the coefficient of oxygen equivalency estimation methods are developed and reported. For LOF_{N₂O} and LEL_{N₂O}, their temperature dependence is given as well, and also compared to those of flammable substance /air mixtures.

1. Introduction

Nitrous oxide is used as an oxidizer in the chemical industry. It is an oxidizer with enhanced oxidizing potential compared to air, but its handling is not as critical as the handling of pure oxygen. Safety characteristics with N₂O as oxidizer differ remarkably from those in air which are mostly well known. The enhanced oxidizing potential of N₂O is reflected by the coefficient of oxygen equivalency which is 0,42 [1, 2], whereas the coefficient of oxygen equivalency of air is 0,209. These coefficients are derived from the respective limiting oxygen fraction of ethane in N₂O with N₂ as inert gas. The aim of the reported investigations was to check whether the coefficient of oxygen equivalency of 0,42 is generally valid to such an extent that it can be used to estimate safety characteristics in N₂O. The investigations covered lower explosion limits (LEL), limiting oxidizer fraction (LOF) and maximum experimental safe gap (MESG), because these characteristics are fundamental in explosion safety.

2. Experimental

Before starting the experiments, it was checked by ignition trials that the self-decomposition of pure N₂O was not activated by the ignition source used.

2.1. Lower explosion limits and limiting oxidizer fraction

The determination of the lower explosion limits (LEL_{N₂O}) and limiting oxidizer fraction (LOF_{N₂O}) with N₂O as an oxidizer was carried out using the experimental set-up according to EN 1839 Method T [3] without any modification. The apparatus was placed in a heating chamber.

The procedure for the determination of the LELs, including the criterion was in accordance with EN 1839 (2003). The concentration of the flammable substance/N₂O mixtures was varied till just no flame detachment was observed. However, it was not

possible to estimate the starting concentration as given in EN 1839 (2003). The LELs have been determined at three temperatures.

The LOFs were determined for N₂ as inert gas. The procedure for the determination of LOF in N₂O was changed to some extent compared to EN 14756 (2006) [4]. The determination of the upper explosion limit was waived. Instead of that, the concentration of the flammable substance /N₂O/inert mixture was changed along the stoichiometric fuel/N₂O ratio till no flame detachment could be observed. In the next step, the amount of flammable substance and inert gas was varied iteratively until just no flame detachment occurred. This iterative procedure was carried out in the range of concentrations richer than stoichiometric, because experience with the determination of the LOC in air has shown that LOC is mostly found at flammable substance concentrations slightly above the stoichiometric concentration.

The LOFs have been determined at three temperatures.

2.2. Maximum experimental safe gap

The maximum experimental safe gap was determined in a modified experimental set-up according to IEC 60079-20-1 (2010) [5]. The modifications are as follows: The glass windows have been replaced by stainless steel plates because of the higher explosion pressure which is generated when N₂O is used as oxidizer. Because of this, it was no longer possible to observe the flame transmission through the gap visually. Therefore, a thermocouple positioned in the outer chamber was used for the detection of a flame transmission. In case of a flame transmission, a steep and high temperature increase is detected with the thermocouple, because the inner and outer chamber is filled with mixtures at, respectively near stoichiometric composition. The apparatus was placed in a heating chamber. The procedure for the determination of the MESGs was in accordance with IEC 60079-20-1 (2010).

3. Results and discussion

3.1. Limiting oxidizer fraction

As can be seen from Table 1 (data at 20 °C), the limiting oxidizer fraction with N₂ as inert gas is mostly more than 50 % higher compared to the LOC for oxygen (air).

Table 1: LOC, LOF_{N₂O} and the ratio LOC/LOF_{N₂O} at 20 °C (Inert N₂)

Substance	LOC [Vol %]	LOF _{N₂O} [Vol %]	LOC/LOF _{N₂O}
Hydrogen	4,3	13,4	0,321
Ethene	7,6	20,3	0,374
Methane	9,9	23,0	0,430
Propane	9,3	22,2	0,419
n-Hexane	9,1	21,7	0,419
Methanol	8,1	18,7	0,433
Ethanol	8,5	21,5	0,395
2-Propanol	8,7	22,0	0,395
Acetone	9,0	22,1	0,407
2-Butanone	8,8	21,3	0,413
Tetrahydrofurane	9,2	21,3	0,432
1,4-Dioxane	7,6	19,9	0,382
Ethyl acetate	9,8	22,4	0,438

The LOF_{N_2O} of hydrogen, ethene and 1,4-dioxane differ more. The average ratio of LOC/LOF_{N_2O} (without H_2) at 20 °C is 0,41 ± 0,021 and 0,0415 ± 0,023 at 100 °C. At higher temperatures an influence of the temperature on the coefficient of oxygen equivalency cannot be excluded (see Table 2). The LOCs in oxygen (air) are taken from the database CHEMSAFE ® [6].

Table 2: LOC/ LOF_{N_2O} ratios at different temperatures

Substance	LOC/ LOF_{N_2O}		
	20°C	100°C	180°C
Hydrogen	0,321	0,315	—
Ethene	0,374	—	—
Methane	0,430	0,454	—
Propane	0,419	0,433	—
n-Hexane	0,419	0,407	—
Methanol	0,433	0,433	—
Ethanol	0,395	0,389	—
2-Propanol	0,395	0,397	—
Acetone	0,407	—	—
2-Butanone	0,413	0,404	0,380
Tetrahydrofurane	0,432	0,419	0,392
1,4-Dioxane	0,382	0,383	0,368
Ethyl acetate	0,438	0,435	0,407

The temperature dependence of the LOF_{N_2O} and the LOC is shown in Table 3.

Table 3: Temperature dependence of LOF_{N_2O} and LOC

Substance	$d(LOC)/dT$ per 100 K [%]	$d(LOF_{N_2O})/dT$ per 100 K [%]
		N_2O
Hydrogen	-18,0	-7,5
Ethene	—	-5,5
Methane	-8,5	-6,5
Propane	-10,1	-5,9
n-Hexane	-11,0	-7,1
Methanol	-10,9	-8,7
Ethanol	-8,8	-6,0
2-Propanol	-8,6	-7,6
Acetone	—	-6,2
2-Butanone	-12,3	-7,0
Tetrahydrofurane	-11,5	-7,0
1,4-Dioxane	-9,3	-7,9
Ethyl acetate	-11,0	-7,0

Some examples are given in Figure 1. As can be seen the data gained allow a linear regression over the temperature range investigated. The inclination of the respective linear regression is more unique with the data in N_2O than with those in oxygen (air) (see Table 3).

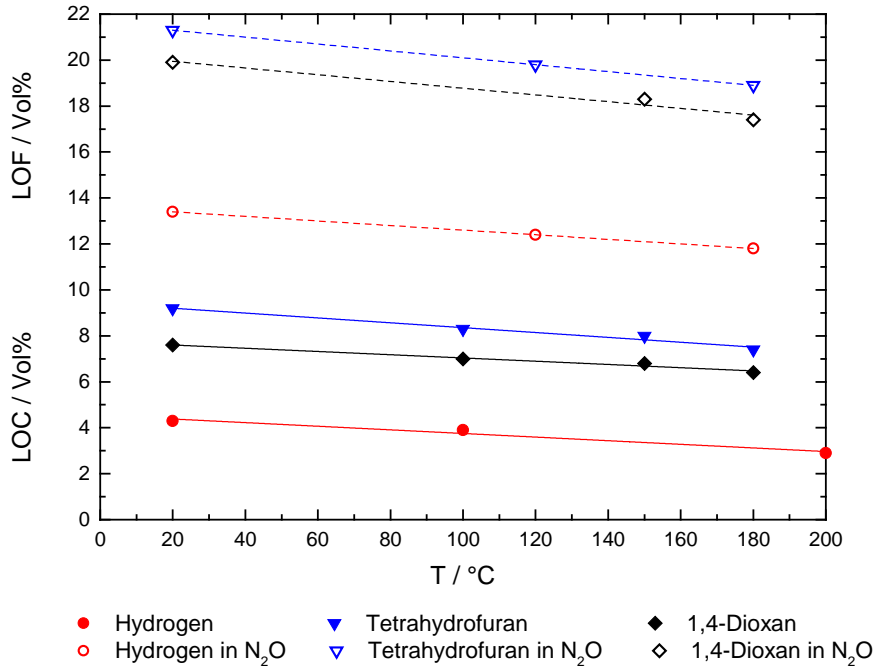


Figure 1: Temperature dependence of the LOF in air (LOC) and N₂O with N₂ as inert

The temperature dependences given are calculated according to

$$\frac{d(LOF)}{dT} = \frac{LOF_{120} - LOF_{20}}{LOF_{20}} \cdot 100\% \quad (1)$$

$$\frac{d(LOC)}{dT} = \frac{LOC_{120} - LOC_{20}}{LOC_{20}} \cdot 100\% \quad (2)$$

3.2.1 Applicability of the coefficient of oxygen equivalency

Figure 2 compares the experimentally determined LOF_{N₂O} with the calculated ones using the coefficient of oxygen equivalency of 0,42 [1].

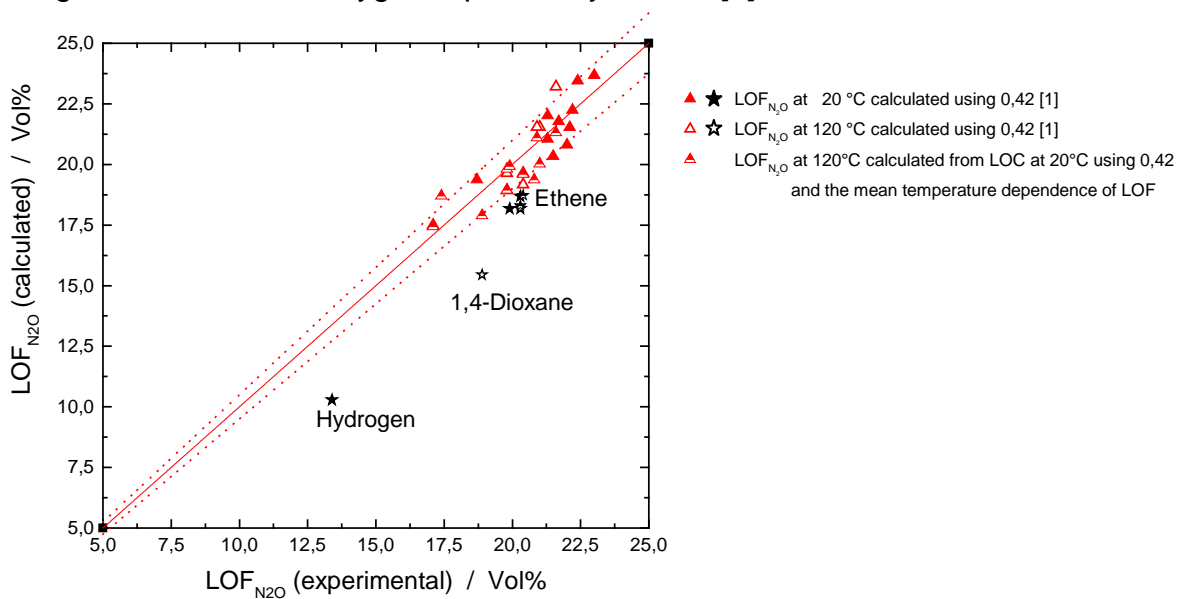


Figure 2: Experimental and calculated LOF_{N₂O}

Allowing for a scatter of $\pm 5\%$ to take into account all uncertainties of measurement (in air and in N_2O), all investigated substances fit the band width except hydrogen, ethene and 1,4-dioxane.

If the LOF_{N_2O} at higher temperatures is of interest, the LOF at 20 °C should be used in combination with a temperature dependence of 8 % per 100 K. Using the respective data in oxygen (air) would result in lower LOFs - but on the safe side - because the temperature dependence of the LOC is higher except for 1,4-dioxane and hydrogen.

3.2. Explosion limits

As expected and shown by some single literature data [7, 8] the LELs in N_2O are significantly lower than those in air.

Table 4 summarizes the LEL_{N_2O} at 20 °C for the investigated substances and compares them to the respective LEL in air (oxygen).

Table 4: LEL in air, LEL in N_2O at 20 °C and ratios of stoichiometric concentration to lower explosion limit in O_2 and N_2O

Substance	LEL_{air,O_2} [Vol %]	Cst_{O_2}	Cst_{O_2}/LEL_{O_2}	LEL_{N_2O} [Vol %]	Cst_{N_2O}	Cst_{N_2O}/LEL_{N_2O}
Hydrogen	4,40	0,33	0,08	2,50	0,50	0,20
Ethene	2,40	0,25	0,10	1,20	0,14	0,12
Methane	4,40	0,33	0,08	1,50	0,20	0,13
Propane	1,70	0,17	0,10	0,76	0,09	0,12
n-Hexane	1,00	0,10	0,10	0,47	0,05	0,11
Methanol	6,00	0,40	0,07	2,33	0,25	0,11
Ethanol	3,10	0,25	0,08	1,30	0,14	0,11
2-Propanol	2,00	0,18	0,09	0,88	0,10	0,11
Acetone	2,50	0,20	0,08	1,04	0,11	0,11
2-Butanone	1,50	0,15	0,10	0,77	0,08	0,11
Tetrahydrofurane	1,50	0,15	0,10	0,77	0,08	0,11
1,4-Dioxane	1,40	0,17	0,12	0,85	0,09	0,11
Ethyl acetate	2,00	0,17	0,08	0,85	0,09	0,11

The LELs in N_2O are lowered between 37,5 % and 65,9 %. The average is 53 %. Hydrogen (-37,5 %), methane (-65,9 %) and 1,4-dioxane (39,3 %) show notably different results compared to the other investigated substances. The average ratio of $LOF_{N_2O}/LEL_{air,O_2}$ (without hydrogen, methane and 1,4-dioxane) is $0,45 \pm 0,06$.

The LELs of the organic compounds in N_2O are however found at about 10 % of the stoichiometric composition as it is with flammable substance/ O_2 mixtures (Table 4).

Table 5 shows that the temperature dependence of the LELs in N_2O varies from -22,0 % per 100 K (2-Propanone) to -27,6 % per 100 K (Hydrogen). Compared to the respective values in air, the temperature dependence in N_2O seems to be more unique. The temperature dependences of the LEL in air for the investigated substances vary between -10,3 % per 100 K (2-Propanol) und -25,3 % per 100 K (Tetrahydrofurane). The temperature dependences are calculated according to

$$\frac{d(LEL)}{dT} = \frac{LEL_{120} - LEL_{20}}{LEL_{20}} \cdot 100\% \quad (3)$$

The values for the LELs in air were taken from the database CHEMSAFE®.

Table 5: Temperature dependence of LEL_{N_2O} and LEL_{air}

Substance	d(LEL)/dT per 100 K [%] O ₂	d(LEL)/dT per 100 K [%] N ₂ O
Hydrogen	-15,4	-27,6
Ethene	— -	25,8
Methane	-13,8	-25,5
Propane	-13,0	-26,0
n-Hexane	-19,0	-25,4
Methanol	-12,7	-26,1
Ethanol	-13,7	-24,5
2-Propanol	-10,3	-24,8
Acetone	-15,2	-22,0
2-Butanone	-21,8	-24,6
Tetrahydrofurane	-25,3	-24,6
1,4-Dioxane	-13,6	-25,6
Ethyl acetate	-12,5	-22,3

3.2.1 Applicability of the coefficient of oxygen equivalency

Figure 3 compares the experimentally determined LEL_{N_2O} at 20 °C with the calculated ones using the coefficient of oxygen equivalency 0,42 at 20 °C [2] or the individual LOC/LOF_{N₂O} ratios (see Table 1).

Allowing for a scatter of ±10% to take into account all uncertainties of measurement (LEL, LOC in air and LEL in N₂O, LOF in N₂O), the calculated LEL of all investigated substances except hydrogen, methane, ethene and 1,4-dioxane fits the band width.

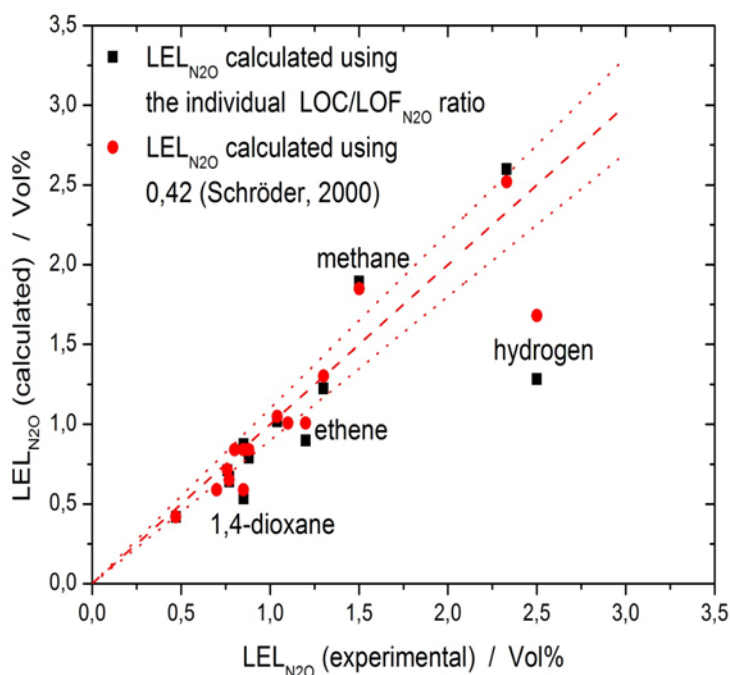


Figure 3: Experimental and calculated LEL_{N_2O} at 20 °C

Although in some cases there is a larger difference between the coefficient of oxygen equivalency according to Schröder and the individual LOF_{N_2O}/LOC ratio, this is without consequences for the calculated LELs with respect to the bandwidth of 10%.

If LEL_{N_2O} at elevated temperatures is of interest, the LEL_{N_2O} at 20°C - either measured or calculated - should be used in combination with a temperature dependence of LEL_{N_2O} of -28 % per 100 K. Using the respective temperature dependences in oxygen (air) would result in some cases in LELs which are not on the safe side (see Figure 4).

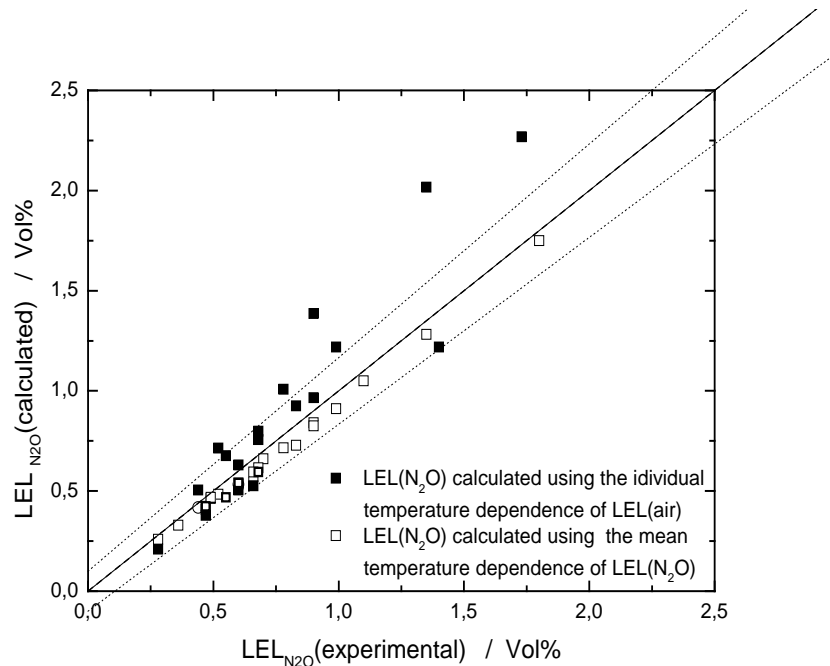


Figure 4: Experimental and calculated LEL at elevated temperatures

3.3. Maximum experimental safe gap

Table 6 summarizes the MESG data in N_2O and the MESG data in air. Skipping the data of hydrogen and ethine, the mean ratio of $MESG_{N_2O}$ to $MESG_{air}$ is $0,43 \pm 0,04$.

Table 6: MESG in air and in N_2O at 20 °C

Substance	$MESG_{air}$ [mm] *)	$MESG_{N_2O}$ [mm]	$MESG_{N_2O}/MESG_{air}$
Ethine	0,37	0,02	0,05
Ethene	0,65	0,24	0,37
Isobutene	0,94	0,43	0,46
Isobutane	0,98	0,39	0,40
Methyl ethyl ketone	0,88	0,43	0,49
Acetone	1,04	0,47	0,45
Ethyl acetate	0,98	0,49	0,50
Cyclopentane	1,01	0,41	0,41
Cyclohexane	0,94	0,42	0,45
n-Hexane	0,93	0,38	0,41
n-Heptane	0,91	0,41	0,45
n-Propane	0,92	0,37	0,40
n-Butane	0,98	0,37	0,38

Table 6: MESG in air and in N₂O at 20 °C (continuing)

Substance	MESG _{air} [mm] *)	MESG _{N₂O} [mm]	MESG _{N₂O} /MESG _{air}
n-Butene	0,94	0,32	0,34
Ethane	0,91	0,36	0,40
Methane	1,14	0,46	0,40
Isopropyl acetate	1,04	0,47	0,45
Ethyl formate	0,91	0,46	0,51
Hydrogen	0,29	0,06	0,21
Methyl propionate	0,94	0,43	0,46
Diethylether	0,94	0,37	0,39
Isopentane	0,87	0,39	0,45
Cyclohexene	0,98	0,36	0,37
Methyl formate	0,94	0,47	0,50
Tetrahydrofurane	0,94	0,37	0,39
n-Pentane	0,87	0,38	0,44
Methyl tert-butyl ether	0,98	0,41	0,42

*) Database CHEMSAFE (2011)

3.3.1 Applicability of the coefficient of oxygen equivalency

Figure 5 compares the experimentally determined MESG_{N₂O} at 20 °C with the calculated ones using the coefficient of oxygen equivalency 0,42 at 20 °C or the individual LEL_{N₂O} ratio (see Table 1). Allowing a scatter of ±0, 03 mm to take into account all uncertainties of measurement (MESG, LOC in air and MESG, LOF in N₂O), the calculated MESG of all investigated substances, except hydrogen, ethane, n-butene, and 1,4-dioxane, fit the bandwidth, respectively are on the safe side.

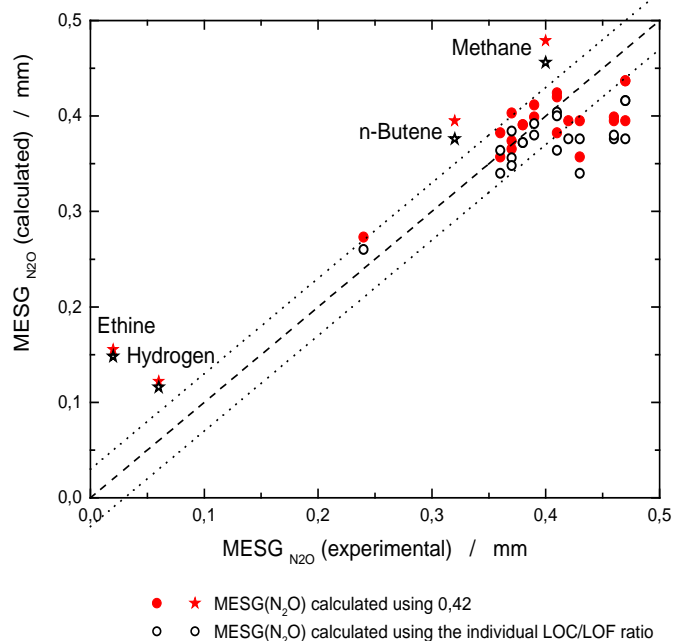


Figure 5: Experimental and calculated MESG

4. Conclusions

Based on the experimental investigations it could be shown that the coefficient of the oxygen equivalency for N₂O [2] can be used to estimate the LEL, LOF and MESG in N₂O for organic substances except for those having self-reactive properties (e.g.

short-chain alkenes, short-chain alkynes) and cyclic ethers. It cannot be used for inorganic substances!

This holds also for data from literature (Table 7).

Table 7: Experimental LEL in N₂O at 20 °C from literature and calculated LEL in N₂O using the coefficient of oxygen equivalency for N₂O

Substance	LEL(experimental) [Vol %]	LEL (calculated) [Vol %]
Ammonia [7]	4,4	6,0
n-Butane [7]	0,7	0,6
Ethane [2]	1,1	1,0
Carbon monoxide[7]	9,5	4,6
Propene [7]	0,8	0,8

It is expected that the estimation of UEL (upper explosion limit) in N₂O using the coefficient of the oxygen equivalency is less successful because at the UEL stoichiometric reactions are not to be assumed as it is with LEL, LOF and MESG.

The temperature dependence of the LEL in N₂O ($\cong -28\%$ per 100 K temperature increase) and LOF in N₂O ($\cong -8\%$ per 100K temperature increase) seems to be more unique than those in air (oxygen). Therefore if data at elevated temperatures are of interest, the estimated value at 20 °C and the respective temperature dependence in N₂O should be used.

The fact that the LELs of organic substances in N₂O are found at about 10 % the stoichiometric composition can be used for a rough estimation too. Furthermore the estimation of a starting concentration when determining the LEL is possible.

When using the discussed estimation methods to get LEL, LOF or MESG in N₂O, a safety margin has to be applied in any case to take into account all uncertainties.

5. Literature

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