1. Hazardous Properties of Materials

1.1 Flammability

A large number of the materials handled in the process industry are flammable. They react with oxygen, releasing thermal energy. In general, the oxygen stems from the air but other oxidants have to be considered as well, for example hydrogen peroxide or ammonium nitrate that easily release oxygen. Furthermore, substances like chlorine or fluorine can play the role of an oxidant.

The consequence of a combustion process is either a fire or an explosion. Which of the possibilities occurs depends on the boundary and environmental conditions of the release (cf. /1/).

Example 1.1: Empirical probabilities for fires and explosions

The data bank ARIA /2/ presents the following numbers of events as a consequence of hydrogen releases in the process industry causing a fire and/or an explosion (including multiple counts): a = 180 events „explosion or fire ", b = 112 events „explosion " and c = 126 events „fire".

Determine the conditional probabilities (the condition is the release whose probability of occurrence is assumed here to be equal to 1) for the different events.

Solution

The sum of the numbers of events with fires and explosions amounts to

$$g = c + b = 238$$

However, this includes events where fire and explosion occurred jointly. Their number is

$$d = g - a = 58$$

In consequence one obtains

$b - d = 54$ events with an explosion only and

and

$c - d = 68$ events with a fire only.

Hence, we obtain the following conditional probabilities:

- only fire:	68/180	= 0.378
- only explosion:	54/180	= 0.300
- fire and explosion:	58/180	= 0.322

1.2 Explosion Limits

Flammable gases and vapours just as flammable dusts can react with an oxidant, e.g. oxygen of the air, such that after ignition the reaction becomes self-propagating and leads to an explosion. This is accompanied by an increase in temperature and pressure.

Combustion can occur only if the mixture of fuel and oxygen lies within a certain range. This is characterised by the lower and upper explosion limits (LEL and UEL). They represent the volume ratio of fuel vapour in air. Below the lower explosion limit the mixture is too lean, above the upper limit it is too rich for a combustion to occur. The explosion limits vary with variations of pressure and temperature (cf. /1/)

The explosion limits depend on a variety of boundary conditions. This is why their measurements result in different values, as illustrated by Example 1.2 for ethylene.

Example 1.2: Uncertainties of the explosion limits taking ethylene as an example

The literature provides the following values for the LEL of ethylene

Lower explosion limit (LEL) of ethylene in vol%							
2.3	2.7	3.1	2.4	2.7	2.8	2.3	2.8

Let us assume the above values represent N = 8 independent measurements (this is often not the case, since values from the same source are quoted in several references). Then the explosion limit may be assumed to be a random variable, i.e. a variable that adopts certain values with a certain probability. Random variables are described by probability distributions. In what follows the logarithmic normal (lognormal) distribution (the logarithms of the original values denoted by x_n are normally distributed, cf. /3/) is used to represent the values. The lognormal distribution is defined on the positive half-axis and therefore suited to represent quantities that can only adopt positive values.

As mean or expected value of the logarithms of the values of x_n one has

$$\mu = \frac{1}{N} \cdot \sum_{n=1}^{N} \ln x_n = 0.9648 \qquad (1)$$

and as the corresponding standard deviation

$$s = \frac{1}{N-1} \cdot \left(\sum_{n=1}^{N} (\ln x_n)^2 - N \cdot \mu^2 \right) = 0.1073 \qquad (2)$$

The pertinent probability distribution and probability density function, simply termed probability and probability density or pdf, are represented by Figure 1.

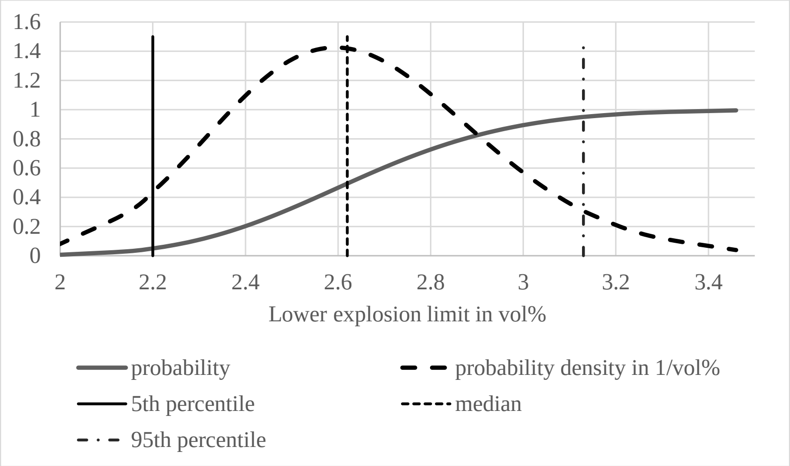

Fig. 1: Probability and probability density of the lower explosion limit of ethylene (expected value: $\exp(\mu+s^2/2) = 2.64$, median: $\lambda_{50} = \exp(\mu)=2.62$, $K_{95} = 1.6449 \cdot s = 0.175$, 5th percentile: $\lambda_{05} = \lambda_{50}/K = 2.20$, 95th percentile: $\lambda_{95} = \lambda_{50} \cdot K = 3.13$)

Example 1.3: Determination of the lower and upper explosion limits of town gas

Town gas had the following main components in the 20th century

Constituent	*Volume fraction in vol%*	*LEL in vol%*	*UEL in vol%*
Carbon monoxide	18	10.9	76
Carbon dioxide	5	-	-
Hydrogen	50	4.0	77
Methane	19	4.4	17
Nitrogen	6	-	-

Which are the values of the lower and the upper explosion limits?

Solution

Since in this case three (I=3) flammable gases are involved that do not react with one another, Le Chatelier's rule is applied. It reads as follows

$$\mathrm{LEL} = \frac{1}{\sum_{i=1}^{I} \frac{x_i}{\mathrm{LEL}_i}} \tag{1}$$

$$\mathrm{UEL} = \frac{1}{\sum_{i=1}^{I} \frac{x_i}{\mathrm{UEL}_i}} \tag{2}$$

In eqs. (1) and (2) x_i denotes the mole fraction of constituent i in the mixture; LEL_i and UEL_i are the corresponding explosion limits. The validity of the ideal gas law is assumed; hence, the volume fraction corresponds to the mole fraction.

According to eqs. (1) and (2) one obtains

$$\mathrm{LEL} = \left(\frac{0.18}{10.9} + \frac{0.5}{4.0} + \frac{0.19}{4.4} \right)^{-1} = 5.41$$

$$\mathrm{UEL} = \left(\frac{0.18}{76} + \frac{0.5}{77} + \frac{0.19}{17} \right)^{-1} = 49.9$$

Experience shows that the above approximation of the lower explosion limit for “similar” flammable gases agrees reasonably well with the experimental values. The approximation for the upper explosion limit exhibits larger deviations. Caution is required in applications to safety problems since the deviations may lie on both, the safe and the unsafe side.

Example 1.4: Determination of the minimum quantity of air for reducing a concentration of propane below the lower explosion limit

A burner is supplied via a pipe DN40 with a mixture of 5vol% of propane and 500Nm^3/h of air (outside diameter 44.5mm, wall thickness 1.85mm).

Mixtures of propane and air within the explosion limits (lower explosion limit (LEL): 1.7vol%, upper explosion limit (UEL): 10.8vol% can be ignited.

In case ignition should fail, the mixture of gas and air would be carried unaltered downstream from the burner. If ignited there an explosion might occur. Therefore, the possibility of injecting additional air is provided for. Thus, the concentration of propane can be reduced to a pre-determined value for which the mixture is too lean to ignite.

The possibility of local gas accumulations is catered for by applying a safety factor of 5 based on VDI 2263, part 6 (analogy). Hence, one assumes that an ignition is possible for mixtures above 20% of LEL, i.e. above LEL* = 0.34vol%. This accounts for the fact that after injection of additional air a homogeneous mixture may not necessarily be formed everywhere and thus LEL may be exceeded in certain sections of the pipe despite a global concentration below LEL.

Datum: The normal volume of a gas (at 0°C and 101325Pa) amounts to V_{nm}=22.414 m^3/kmol

Solution

The incoming mass flow is composed of the following constituents

$$\dot{n}_{C3H8} = \frac{0.05 \cdot 500\,m^3/h}{22.414\,m^3/kmol} = 1.1154\,kmol/h \text{ of propane and} \tag{1}$$

$$\dot{n}_{air} = \frac{0.95 \cdot 500\,m^3/h}{22.414\,m^3/kmol} = 21.1921\,kmol/h \text{ of air} \tag{2}$$

In order to lower the concentration in the mixture to LEL* an additional flow of air, $\dot{n}_{z,air}$, is injected. It is obtained from

$$LEL* = \frac{\dot{n}_{C3H8}}{\dot{n}_{C3H8} + \dot{n}_{air} + \dot{n}_{z,air}} \tag{3}$$

Rearranging eq. (3) gives

$$\dot{n}_{z,air} = \frac{\dot{n}_{C3H8} \cdot (1 - LEL*) - \dot{n}_{air} \cdot LEL*}{LEL*} = \frac{1.1154\,kmol/h \cdot (1 - 0.0034) - 21.1921\,kmol/h \cdot 0.0034}{0.0034}$$
$$= 305.75\,kmol/h$$

This corresponds to 6853.1Nm^3/h. However, it should be observed that the injection of additional air is only necessary as long as the supply of the mixture is not stopped.

Example: 1.5: Avoiding an explosion while removing residual ethanol

Residual ethanol (10kg) is to be removed from an equipment by making nitrogen pass through it. Nitrogen pressure amounts to p = 1.5bar, and its temperature, applicable to the ethanol as well, is ϑ = 40°C. After passing through the equipment the volume flow rate of nitrogen and absorbed ethanol is mixed with a flow rate of air of $\dot{n}_L$ = 1.115mol/s at 20°C.

The volume flow rate $\dot{V}$ or the molar flow rate $\dot{n}$, respectively, are to be determined such that on maximum intake of ethanol by nitrogen (i.e. reaching the concentration of saturation) 20% of the lower explosion limit of ethanol in air (3.1vol%), i.e. LEL* = 0.2·0.031 = 0.0062, is not exceeded.

Data: M_{C2H6O}: molar mass of ethanol (46.07g/mol); M_{air}: molar mass of air (28.96 g/mol); M_{N2}: molar mass of nitrogen (28.01g/mol); ρ_{air} : density of air (1.2kg/m^3)

Solution

In terms of an equation the requirement is that $\dot{n}$ is to be determined such that

$$\frac{\dot{n}\cdot x}{\dot{n}\cdot x+\dot{n}\cdot(1-x)+\dot{n}_{air}}=LEL^{*} \tag{1}$$

is satisfied. In eq. (1) the following notation is used:

$\dot{n}$:	molar flow rate of nitrogen + ethanol in mol/s
$\dot{n}_{air}$:	molar flow rate of air in mol/s
$\dot{n}\cdot x$:	molar flow rate of ethanol in mol/s
$\dot{n}\cdot(1-x)$:	molar flow rate of nitrogen in mol/s
x:	mass fraction of ethanol in the flow (x = 0.1202, see below)

In order to determine $\dot{n}$ the mass fraction of ethanol, x, must be calculated. This fraction depends on the concentration of saturation of ethanol in nitrogen, which, in turn, depends on the saturation pressure. The fraction is

$$x=\frac{\rho_{C2H6O}/M_{C2H6O}}{\rho_{C2H6O}/M_{C2H6O}+\rho_{N2}/M_{N2}} \tag{2}$$

The densities in the mixture ethanol/nitrogen in eq. (2) result from (cf. /4/)

$$\rho_{C2H6O}=\frac{p_{sat}}{R_{C2H6O}\cdot T} \qquad \text{and} \qquad \rho_{N2}=\frac{p-p_{sat}}{R_{N2}\cdot T} \tag{3}$$

with

p_{sat}: saturation pressure of ethanol at 1.5 bar and 40°C
R_{C2H6O}: specific gas constant of ethanol (180.47J/(kg K)):
R_{N2}: specific gas constant of nitrogen (296.8J/(kg K))
T: absolute temperature of ethanol (T= 273.15K+ 40 K =313.15K)

The saturation pressure p_{sat} in eq. (4) is obtained according to /4/ from

$$p_{sat} = p^*_{sat} \cdot \exp\left[v_k / \left(R_{C2H6O} \cdot T\right) \cdot \left(p - p^*_{sat}\right)\right], \qquad (4)$$

with

p^*_{sat}: saturation pressure of ethanol at 1bar and 40°C (0.1799bar)

p_{sat}: saturation pressure of ethanol at 1.5bar and 40°C (0.1804bar)

v_k: specific volume of the ethanol condensate at 1.5bar and 40°C (0.00128m^3/kg)

Saturation pressure

According to eq. (4) one obtains on applying the data of the problem

$$p_{sat} = p^*_{sat} \cdot \exp\left[v_k / \left(R_{C2H6O} \cdot T\right) \cdot \left(p - p^*_{sat}\right)\right] = 0.1799\,\text{bar}$$

$$\cdot \exp\left[\frac{0.00128\,\text{m}^3/\text{kg}}{180.47\,\text{J}/\left(\text{kgK}\right) \cdot 313.15\,\text{K}} \cdot \left(150000 - 17990\right)\text{Pa}\right] = 0.18044\,\text{bar}$$

Densities

According to eq. (3) one obtains

- for ethanol $\rho_{C2H6O} = \dfrac{p_{sat}}{R_{C2H6O} \cdot T} = \dfrac{18044\,\text{Pa}}{180.47\,\text{J}/\left(\text{kgK}\right) \cdot 313.15\,\text{K}} = 0.319\dfrac{\text{kg}}{\text{m}^3}$

- for nitrogen $\rho_{N2} = \dfrac{p - p_{sat}}{R_{N2} \cdot T} = \dfrac{150000\,\text{Pa} - 18044\,\text{Pa}}{296.8\,\text{J}/(\text{kg}\,\text{K}) \cdot 313.15} = 1.42\dfrac{\text{kg}}{\text{m}^3}$

Determination of the mass fraction of ethanol according to eq. (2)

$$x = \frac{\rho_{C2H6O} / M_{C2H6O}}{\rho_{C2H6O} / M_{C2H6O} + \rho_{N2} / M_{N2}} = \frac{0.319\,\text{kg}/\text{m}^3 / 46.07\,\text{kg}/\text{kmol}}{0.319\,\text{kg}/\text{m}^3 / 46.07\,\text{kg}/\text{kmol} + 1.42\,\text{kg}/\text{m}^3 / 28.01\,\text{kg}/\text{kmol}}$$

$$= 0.1202$$

Determination of the molar flow rate of ethanol and nitrogen

After isolating the molar flow rate eq. (1) becomes

$$\dot{n} = \frac{\dot{n}_L \cdot LEL^*}{x - LEL^*} = \frac{1.115\,mol/s \cdot 0.0062}{0.1202 - 0.0062} = 0.0606\,\frac{mol}{s}$$

The mass fractions in the mixture of air, nitrogen and ethanol are obtained as the quotients of the respective molar flow rates and the total flow rate. Assuming the applicability of the ideal gas law, the following volumetric fractions are calculated

• mass fraction of ethanol	0.0062
• mass fraction of nitrogen	0.0454
• mass fraction of air	0.9484

The values lie below the flammable zone (cf. Abb. 1).

Converting the above quantities into hourly mas flow rates one obtains:

Mass flow rate of ethanol:	1.21kg/h
Mass flow rate of nitrogen:	5.38kg/h
Mass flow rate of air:	116.20kg/h

The ethanol is eliminated after 8.26h.

1.3 Minimum Ignition Energy

The minimum ignition energy (MIE) is a parameter for judging the incendivity of important sources of ignition such as electrostatic discharge and mechanical spark. It represents the smallest possible amount of energy capable of just igniting the most flammable gas/air or vapour/air mixture in such a way that a flame occurs that is not restricted to the immediate vicinity of the igniting spark. Knowledge of the MIE is required for applying the explosion protection measure ”avoidance of effective ignition sources”. The MIE is determined under well-defined experimental conditions. It is the smallest amount of energy stored in a capacitator that produces a spark sufficient to ignite the most flammable mixture of a flammable atmosphere. The MIE is stated in mJ (millijoule).

The minimum ignition energy is determined according to

$$E = \frac{C \cdot U^2}{2} \tag{1}$$

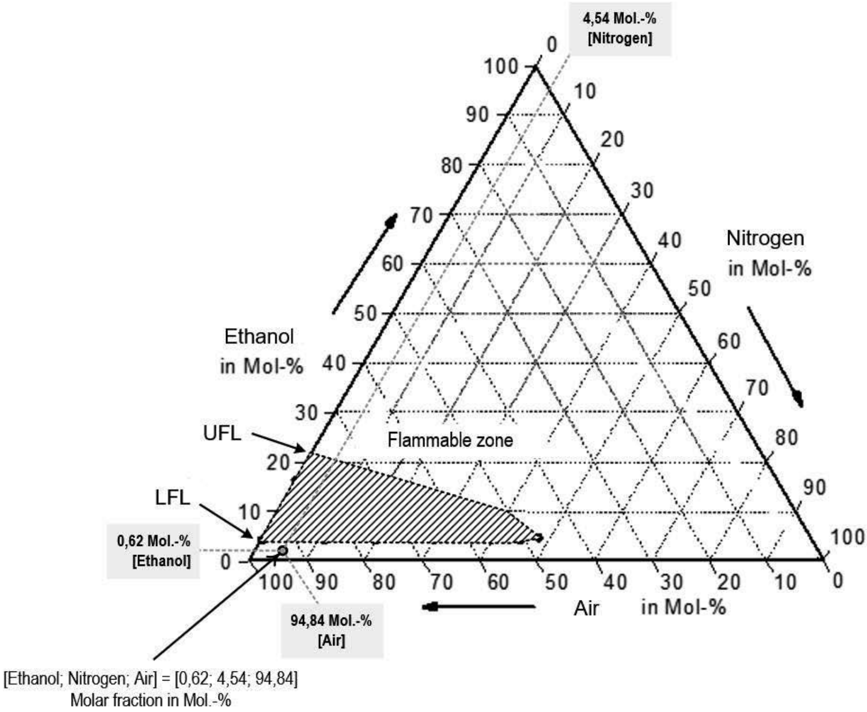

Fig. 1 Ternary diagram for a mixture of ethanol-nitrogen-air (based on /5/)

In eq. (1) E is the ignition energy in J, C the capacitance of the capacitor in Farad $(1\text{F} \mathrel{\hat{=}} 1\text{J/V}^2)$ and U the voltage applied to the capacitor in V. By varying the energy E the energy amount is identified that is just sufficient to ignite the mixture under examination, the MIE.

Example 1.6: Ignition of hydrogen or methane

A capacitor with a capacitance of 560pF (1pF = 10-12 F) is charged with a definite current of U_0 = 220V. Would its discharge ignite hydrogen or methane (MIE_{H2} = 0.012mJ, MIE_{CH4} = 0.29mJ)?

Solution

By substituting the numerical values in eq. (1) one obtains

$$E = \frac{600 \cdot 10^{-12}\,F \cdot (220\,V)^2}{2} = 0.0145\ mJ$$

Since 0.0145mJ > 0.012mJ, but < 0,29mJ ignition would be expected in the case of hydrogen but not with methane.

Example 1.7: Ignition of ethanol and benzene

A capacitor with a capacitance of C = 12000pF (1pF = 10^{-12}F) is charged with a definite current of U_0 = 220V. Benzene vapour (4kg) and ethanol vapour (3kg), respectively, penetrate a room displacing air and forming a homogeneous mixture. The temperature in the room amounts to 25°C, and the pressure is 1bar. Would a discharge of the capacitor ignite ethanol or benzene?

Data: $MIE_{benzene}$ = 0.2mJ; $MIE_{ethanol}$ = 0.28mJ; $LEL_{benzene}$ = 1.2vol%; $LEL_{ethanol}$ = 3.4vol%: $M_{benzene}$ = 78.11g/mol; $M_{ethanol}$ = 46.068g/mol; M_{air}= 28.965g/mol; ρ_{air} = 1.1688kg/m^3; molar volume V_m= 24.78m^3/kmol

Solution

The above data lead to the following concentrations:

- benzene: $m_B = 4000\ g/100\ m^3 = 40\ g/m^3$
- ethanol: $m_E = 3000\ g/100\ m^3 = 30\ g/m^3$

Determination of the volume fractions

The atmosphere in the room contains:

- benzene: $n_B = m_B/M_{Benzol} = 40/78.11 = 0.512\ mol/m^3$
- ethanol: $n_E = m_E/M_{Ethanol} = 30/46.068 = 0.651\ mol/m^3$
- air: $n_L = \rho_{air}/ M_{air} = 1168.8/28.965 = 40.352\ mol/m^3$

Hence, we have the following molar respectively volume fractions:

- benzene: $n_B/[n_B + (n_L - n_B)] = n_B/n_L = 1.269$vol%
- ethanol: $n_E/[n_E + (n_L - n_E)] = n_E/n_L = 1.613$vol%

Substitution of the numerical values in eq. (1) yields