
2.1 Flammability

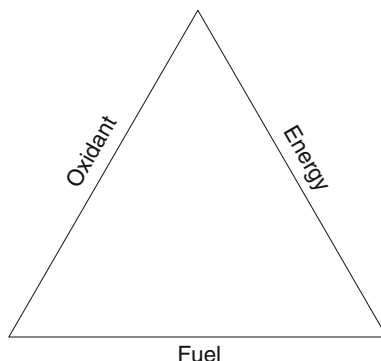
A large number of the materials handled in the process industry are flammable. They react with oxygen releasing thermal energy. In general the oxygen stems from the air but other oxidants have to be considered as well, for example hydrogen peroxide or ammonium nitrate, which easily release oxygen. Furthermore,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

In general combustion takes place if a flammable material enters into contact with an energy source, e.g. an electrical spark or a hot surface, and thus receives energy. If solid or liquid materials are concerned their temperature has to be raised first to such an extent that vapour is produced by vaporization or disintegration. These vapours can form flammable mixtures with air just as flammable gases. If the energy supply is sufficient a self-sustaining exothermic reaction occurs.

The conditions for a combustion process are shown in Fig. 2.1. It presents the so-called fire triangle, which comprises the necessary elements of a combustion process, namely “fuel”, “oxidant” and “energy”.

The consequence of a combustion process is either a fire or an explosion. Which of the possibilities occurs depends on the boundary conditions to be treated below. In general the approach is empirical. For example conditional probabilities (the condition is the preceding release) of 0.6 for a fire and 0.4 for an explosion after the release of a flammable gas or liquid are given in [1].

The safe handling of flammable materials requires the knowledge of their properties, which are normally described by safety parameters. These parameters are not, as a rule, constants of nature but values which are determined under fixed boundary conditions. This leads to the use of standardized measuring apparatuses (vid. [2–4]). When employing these parameters to judge real situations an eye must therefore be kept on the prevailing boundary conditions.

Fig. 2.1 Fire triangle*Example 2.1* Empirical frequencies for fires and explosions

The data bank ARIA indicates the following numbers of events as a consequence of hydrocarbon releases: $a = 1,748$ events “explosion or fire”, $b = 656$ events “explosion” and $c = 1,554$ 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

$$g = c + b = 2,210$$

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

$$d = g - a = 462$$

From this we have

$b - d = 194$ events with an explosion only and

$c - d = 1,092$ events with a fire only.

Hence we obtain the following conditional probabilities:

- Only fire: $1,092/1,748 = 0.625$
- Only explosion: $194/1,748 = 0.111$
- Fire and explosion: $462/1,748 = 0.264$

If the explosion is considered the dominating event and the probability for “fire and explosion” is added to the probability for “only explosion” the result is in good agreement with that of [1]. □

2.1.1 Safety Parameters for Flammable Gases and Vapours

2.1.1.1 Explosion Limits

Combustion can occur only if the mixture of fuel and oxygen lies within a certain range. This is described by the lower and upper explosion limits (LEL and UEL). In older references these limits are referred to as the lower and upper limits of flammability (LFL and UFL) (vid. [4]). They represent the volume ratio¹ of fuel vapour in air. Below the lower explosion limit the mixture is too lean, above the upper limit it is too rich for combustion to occur. The explosion limits are not fixed values. They depend on whether we deal with a mixture with air or with oxygen. Furthermore they are influenced by (vid. [4, 5]):

- pressure,
- temperature,
- direction of flame propagation,
- type and location of the source of ignition, in particular ignition energy,
- type and size of the space (closed, open, geometry),
- possibly the amount of inert gas in the mixture,
- flow regime of the gas,
- gravitational field.

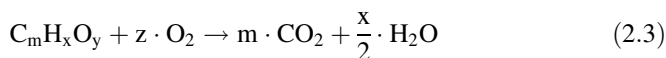
Additionally they depend, as already mentioned, on the boundary conditions of their measurement, as illustrated by Table 2.1. In general the most flammable mixture is close to but not exactly equal to the stoichiometric one [5].

The explosion limits may be calculated approximately by (vid. [6])

$$\text{LEL} = 0.55 \cdot c_{\text{st}} \quad (2.1)$$

$$\text{UEL} = 3.50 \cdot c_{\text{st}} \quad (2.2)$$

In Eqs. (2.1) and (2.2) c_{st} is the stoichiometric concentration (volume percent of fuel in air). In case of a stoichiometric equation of combustion of the form



we have

$$z = m + \frac{x}{4} - \frac{y}{2} \quad (2.4)$$

¹ Strictly speaking the indication of a volume ratio only makes sense at low pressures. At higher pressures the real gas behaviour must be taken into account; hence in that case often mass proportions (mol %) are used.

Table 2.1 Upper and lower explosion limits according to different sources

Stoff	Nabert et al. [7]		Mannan [5]		Coward and Jones [8]	
	Lower explosion limit in Vol%	Upper explosion limit in Vol%	Lower explosion limit in Vol%	Upper explosion limit in Vol%	Lower explosion limit in Vol%	Upper explosion limit in Vol%
Acetone	2.5	14.3	2.6	13	3	11
Acetylene	2.3	78–100	2.5	100	2.5	81
Ammonia	15.4	33.6	15	28	15	28
Benzene	1.2	8.6	1.4	8	1.4	7.1
n-Butane	1.4	9.3	1.8	8.4	1.9	8.5
Carbon monoxide	10.9	76	12.5	74	12.5	74
Cyclohexane	1.1	8.3	1.3	7.8	1.3	8
Ethane	2.5	15.5	3.0	12.4	3.0	12.5
Ethylene	2.3	32.4	2.7	36	3.1	32
Ethylene oxide	2.6	100	3	100	3.0	80
Hydrogen	4.0	77	4.0	75	4.0	75
Methane	4.4	17	5.0	15.0	5.3	14
Propane	1.7	10.9	2.1	9.5	2.2	9.5
Propylene	2.0	11.1	2.4	11	2.4	10.3
Styrene	1.1	6.1	1.1	6.1	1.1	6.1
Toluene	1.1	7.8	1.3	7.0	1.4	6.7

and hence

$$c_{st} = \frac{100}{1 + z/0.21} \quad (2.5)$$

However, Example 2.2 shows that the differences between calculated and measured values are considerable. Hence, whenever possible measured values are to be used.

This applies as well for the pressure dependence of the explosion limits. The following logarithmic relationship is given for the pressure dependence of the UEL (vid. [6])

$$UEL_p = UEL_{0.1\text{MPa}} + 20.6 \cdot (\log p + 1) \quad (2.6)$$

In Eq. (2.6) p denotes the absolute pressure in MPa. The equation does not represent the measured values, as is evident from Table 2.2. The values for 1 bar agree because they are introduced into the equation as the reference value $UEL_{0.1\text{MPa}}$.

Table 2.2 Dependence of the explosion limits on initial pressure (measured values from [4], calculated values (bold print) according to Eq. (2.6))

Material	LEL in vol%			UEL in vol%		
	1 bar	10 bar	100 bar	1 bar	10 bar	100 bar
Hydrogen	4.3	4.9	5.8	78.5	72.4	74
				78.5	99.1	119.7^a
Carbon monoxide	13.1	15.6	17.0	75.9	69.4	68.0
				75.9	96.5	117.1^a
Methane	4.6	5.0	4.3	16.6	21.8	44.7
				16.6	37.2	57.8
Ethane	2.7	2.7	2.7	14.1	19.3	45.2 ^b
				14.1	34.7	55.3

^asince 100 % is the maximum, the value is merely a formal result^bmeasured at an initial pressure of 50 bar

According to [4] the lower explosion limit decreases slightly with increasing initial pressure whilst the upper limit increases strongly. Exceptions from this rule are the gases hydrogen and carbon monoxide. The lower explosion limit of hydrogen at first rises slightly with increasing initial pressure and then decreases with further pressure increase. In the case of carbon monoxide the range between the explosion limits narrows at first with increasing initial pressure and remains constant with a further increase.

With an increase in temperature the range between the lower and upper explosion limits widens for all flammable gases. The relative change of the lower and upper limits is similar for many flammable gases. Hence, it may well be approximated by the following linear relationship

$$x_B(T) = x_B(T_0) \cdot [1 \pm K(T - T_0)] \quad (2.7)$$

In Eq. (2.7) $x_B(T)$ denotes the volume ratio of the gas at temperature T and $x_B(T_0)$ that at the reference temperature T_0 , e.g. ambient temperature. The positive sign applies to the upper explosion limit, the negative sign to the lower limit (vid. [4]). Factors for K are given in Table 2.3, where K_L applies to the lower limit and K_U to the upper.

The above considerations apply to a mixture of a single flammable gas and air. If several gases, e.g. I, are involved which do not react with one another, the principle of Le Chatelier is invoked and we obtain

$$LEL = \frac{1}{\sum_{i=1}^I \frac{y_i}{LEL_i}} \quad (2.8)$$

Table 2.3 Temperature coefficients K_L and K_U for selected flammable gases (vid. [9])

Flammable gas	K_L (LEL) in K^{-1}	K_U (UEL) in K^{-1}	LEL (0 °C)* in mol%	UEL (0 °C)* in mol%
Methane ^a	0.00162	0.00111	4.60	15.64
Ethane ^b	0.00124	0.00098	2.48	14.02
Propane ^b	0.00128	0.00107	1.82	10.57
Isobutane ^b	0.00149	0.00064	1.48	9.18
Hydrogen ^a	0.00162	0.00042	4.18	74.75
Carbon monoxide ^a	0.00138	0.00035	12.07	76.37

*Calculated from experimental data for use in Eq. (2.7)

^aTemperatures up to 400 °C

^bTemperatures up to 250 °C

$$UEL = \frac{1}{\sum_{i=1}^I \frac{y_i}{UEL_i}} \quad (2.9)$$

In Eqs. (2.8) and (2.9) y_i is the molar fraction of material i in the total mixture; LEL_i and UEL_i are the corresponding explosion limits.

Experience tells that this estimate agrees fairly well with the measured values of the lower explosion limit for “similar” flammable gases. The upper limit shows larger deviations. The equations should be applied with care to safety technological questions, since the deviations may lie on both the safe and the unsafe side [4].

Example 2.2 Uncertainties of the explosion limits taking propane as an example

The explosion limits of a material depend on numerous boundary conditions. Hence different measurements result in different values as shown in what follows taking the lower explosion limit of propane as an example. The following values in volumetric percent are given

x_n : 1.7; 2.1; 2.2; 2.1; 2.1; 1.7; 2.1.

Let us assume they represent $N = 7$ 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 which adopts certain values with a certain probability. Random variables are described by probability distributions (vid. Appendix C). In what follows the logarithmic normal (lognormal) distribution (vid. Sect. 9.3.4) is used to represent the values

As mean value of the logarithms of the values of x_n we have

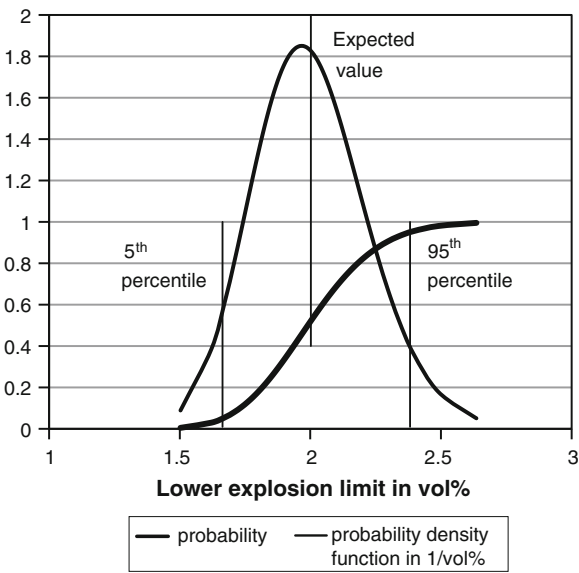
$$\mu = \frac{1}{N} \cdot \sum_{n=1}^N \ln x_n = 0.6882$$

and as the corresponding standard deviation

$$s = \left[\frac{1}{N - 1} \cdot \left(\sum_{n=1}^N (\ln x_n)^2 - N \cdot \mu^2 \right) \right]^{\frac{1}{2}} = 0.1090$$

The pertinent probability distribution and probability density function, simply termed probability and probability density or pdf, are represented by Fig. 2.2.

Fig. 2.2 Probability and probability density of the lower explosion limit of propane



The percentiles are to be interpreted such that the corresponding percentage of the lower explosion limit lies below the respective percentile value. □

Example 2.3 Determination of the lower and upper explosion limits

Determine the lower and upper explosion limits of acetylene, hydrogen and ammonia for a pressure of 1 bar.

Solution

The solution is based on Eqs. (2.1)–(2.5). The results are compiled in Table 2.4.

Table 2.4 Calculation of the lower and upper explosion limits for several materials

Material	Molecular formula	z	c _{st} in vol%	LEL in vol%	UEL in vol%
Acetylene	C ₂ H ₂	2.5	7.749	4.3	27.1
Hydrogen	H ₂	0.5	29.577	16.3	100
Methane	CH ₄	2	9.502	5.2	33.3

Comparison with the measured values from Table 2.1 shows that the results are merely approximations. This underlines that it is necessary from a safety point of view to use measured values. □

Example 2.4 Temperature dependence of explosion limits

The lower and upper explosion limits of methane are to be determined for the temperatures 100, 200, 300 and 400 °C.

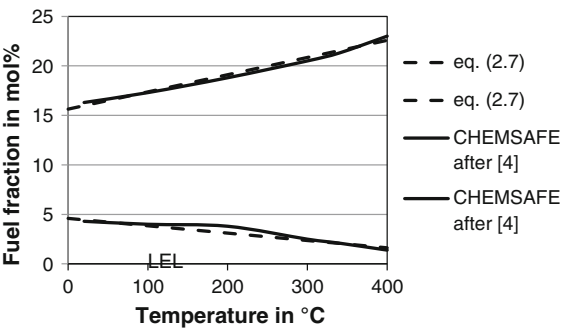
Solution

Combination of Eq. (2.7) with Table 2.3 leads to the results of Table 2.5. They are in good agreement with the measured values, as is demonstrated in Fig. 2.3.

Table 2.5 Temperature dependence of the explosion limits of methane

Methane	0 °C	100 °C	200 °C	300 °C	400 °C
LEL in mol%	4.60	3.85	3.11	2.36	1.62
UEL in mol%	15.64	17.38	19.11	20.85	22.58

Fig. 2.3 Comparison of the temperature dependence of measured and calculated explosion limits of methane



Example 2.5 Calculation of the lower and upper explosion limits of natural and petroleum gas

Natural and petroleum gas have the main components given in Table 2.6.

Table 2.6 Composition of natural and petroleum gas in mol%

	Natural gas	Petroleum gas
Methane	90	–
Ethane	6	–
Propane	2	30
Butane	–	70
Carbon dioxide	1	–
Nitrogen	1	–

Determine their lower and upper explosion limits.

Solution

According to Eqs. (2.8) and (2.9) we obtain

$$\text{LEL} = \left(\frac{0.9}{4.4} + \frac{0.06}{2.5} + \frac{0.02}{1.7} \right)^{-1} = 4.16$$

$$\text{UEL} = \left(\frac{0.9}{17} + \frac{0.06}{15.5} + \frac{0.02}{10.9} \right)^{-1} = 17.05$$

for natural gas and

$$\text{LEL} = \left(\frac{0.3}{1.7} + \frac{0.7}{1.4} \right)^{-1} = 1.48$$

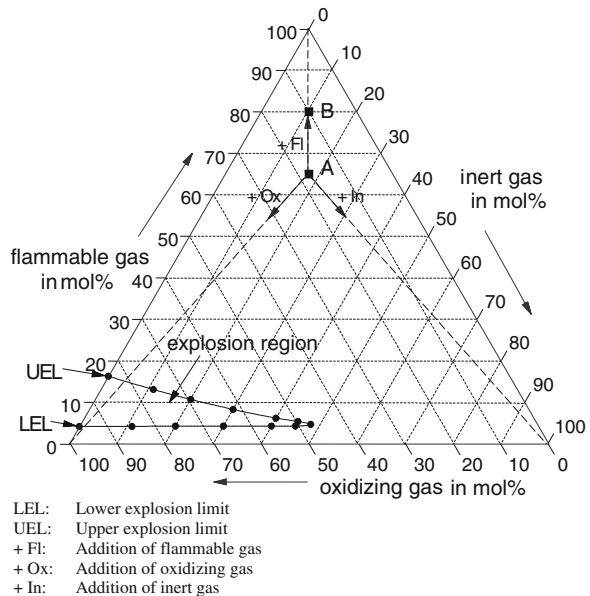
$$\text{UEL} = \left(\frac{0.3}{10.9} + \frac{0.7}{9.3} \right)^{-1} = 9.73$$

for petroleum gas.

2.1.1.2 Explosion Limits for Mixtures

Mixtures of flammable gases and oxidant were treated in the preceding Section. In practice often mixtures have to be assessed which in addition contain an inert gas. The corresponding situation is represented by Fig. 2.4. It is subsequently described following [9].

Fig. 2.4 Explosion region of a flammable gas presented in triangular coordinates [9]



The explosion limits form a boundary line enclosing all flammable compositions; the explosion range contains all flammable mixtures. Points on the sides of the triangle represent two-component systems because the fraction of the third component is zero there. Pure substances are represented by the corner points of the triangle. The fractions of the remaining two components are equal to zero there. In Fig. 2.4 the upper corner represents the pure flammable gas, the lower right corner the pure inert gas and the lower left corner the pure oxidant. If a certain amount of flammable gas, inert gas or oxidant is added to the mixture “A”, a new mixture results. If the component is added continuously, the point “A” moves along a straight line in the direction of one of the corners of the diagram (denoted by the arrows in Fig. 2.4). For example, if a certain quantity of flammable gas is added, a new composition according to point “B” is obtained after the mixture has homogenized.

2.1.1.3 Ignition Temperature

According to [7] the ignition temperature of a flammable gas or flammable liquid is determined in a standardized experimental set-up (vid. [10]). It is the lowest temperature (in °C) of the heated glass bulb, on whose concave wall the inhomogeneous gas air or vapour air mixture of the examined material (at a pressure of 1,013 mbar) is just ignited showing flames (readily ignitable mixture). Hence, it constitutes an appropriate measure for the propensity of materials to be ignited on hot surfaces. This enables one, amongst others, to assign materials to temperature classes according to safety technological criteria.

It must be emphasized that we deal with a measurement which requires no further energy source in order to produce an ignition. Table 2.7 gives ignition temperatures for selected materials.

Table 2.7 Ignition temperatures (from [7])

Material	Ignition temperature in °C	Material	Ignition temperature in °C
Acetone	535	Ethylene	425
Acetylene	305	Ethylene oxide	440
Ammonia	630	Hydrogen	560
Benzene	555	Methane	595
n-Butane	365	Propane	470
Carbon monoxide	605	Propylene	455 ^a
Cyclohexane	260	Styrene	490
Ethane	515	Toluene	545

^aValue for coarse orientation

2.1.1.4 Minimum Ignition Energy

The minimum ignition energy (MIE) is a parameter for judging the incendiarity by 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

which is not restricted to the immediate vicinity of the igniting spark. The value of the MIE depends on both the testing apparatus and the testing procedure. It is determined on the basis of the energy of the discharge spark of a capacitor which is applied to the most flammable mixture under standard conditions (20 °C and 1,013 mbar) [11]. The most flammable mixture is considered to lie in the range of 0.9–1.4 (according to other sources 0.8–2) times the stoichiometric mixture (vid. [3]). The latter can be calculated according to Eq. (2.5).

The minimum ignition energy is determined according to

$$E = \frac{C \cdot U^2}{2} \quad (2.10)$$

In Eq. (2.10) E is the ignition energy in J, C the capacitance of the capacitor in Farad and U the voltage applied to the capacitor in V. By varying the energy E the energy amount is identified which is just sufficient to ignite the mixture under examination, the MIE.

If the ignition source is not at rest relative to the surrounding mixture, for example in the case of a flowing medium, heat is lost and the MIE increases [6]. Table 2.8 contains values of the MIE for selected materials.

Example 2.6 Ignition of hydrogen

A capacitor with a capacitance of 560 pF ($1\text{pF} = 10^{-12}\text{ F}$) is charged with a definite current of $U_0 = 220\text{ V}$. Would its discharge ignite hydrogen?

Solution

$$U(t) = U_0 \cdot \left(1 - e^{-t/\tau_0}\right)$$

describes the time-dependent voltage in the capacitor, $U(t)$, and τ_0 the time constant of the charging system. For simplicity's sake the asymptotic voltage of the capacitor is used. It amounts to U_0 and is obtained in theory for $t \rightarrow \infty$ and in practice after a period of time of approximately five times the time constant.

Table 2.8 Minimum ignition energies (MIEs) for normally ignitable materials (standard conditions) (from [3])

Material	MIE in mJ	Material	MIE in mJ
Methane	0.29–0.31	Pentane	0.22–0.28
Propylene	0.27	Benzene	0.21–0.22
Propane	0.24–0.27	Methanol	0.14
Butane	0.25–0.27	Hydrogen sulphide	0.068
Ethane	0.25	Acetylene	0.019–0.051
Heptane	0.24	Hydrogen	0.012–0.019
Hexane	0.23–0.25	Carbon disulphide	0.009–0.03

Inserting the numerical values in Eq. (2.10) we obtain

$$E = \frac{560 \cdot 10^{-12} \cdot 220^2}{2} = 0.0136 \text{ mJ}$$

Since $0.0136 \text{ mJ} > 0.012 \text{ mJ}$ (lower limit of the interval indicated in Table 2.8) the cautious analyst should expect ignition to occur.

2.1.1.5 Burning Velocity

According to [11] the burning velocity is the movement of the flame front in a homogeneous gas/air mixture per unit of time in vertical direction to the flame front into the unburnt mixture. The burning velocity is determined by heat conduction, diffusion and the flow process with the latter resulting from the expansion of the combustion gases. It depends on the initial temperature, the amount of oxygen introduced, the degree of mixture and catalytic effects (e.g. traces of steam, smoke or dust). The burning velocity is measured with respect to the unburnt gas. Hence, it differs from flame speed which is the velocity of the flame front with respect to a fixed observer. It is usually one or two orders of magnitude higher than the laminar burning velocity because of the acceleration produced by the expanding combustion products.

The burning velocity is usually determined on pre-mixed flames from a Bunsen burner in laminar flow regime (see Sect. 2.1.1.7). It is then called laminar burning velocity. In case of turbulent flow the burning velocity is many times the laminar burning velocity and does not depend on the properties of the mixture alone. Within the explosion limits the burning velocity is an appropriate parameter for describing flame propagation. Burning velocities depend on pressure and temperature [5]. Table 2.9 presents laminar burning velocities for selected substances. In some cases these velocities may be represented by polynomials, as

Table 2.9 Laminar burning velocities for selected materials

Material	v_{burn} in cm s^{-1} cit. according to [5]	v_{burn} in cm s^{-1} cit. according to [12]
Acetylene	173	155
Benzene	40.7	–
n-Butane	40.5	–
Ethane	40.1	47.6
Ethylene	68.8	73.5
n-Hexane	38.5	–
Methane	36.4	44.8
Propane	45	46.4
Hydrogen	320	325

$$v_{\text{burn}} = 4.407 \cdot \phi^3 - 150.69 \cdot \phi^2 + 308.62 \cdot \phi - 122.7 \quad (0.7 < \phi < 1.4) \quad (2.11)$$

for liquefied petroleum gas (LPG) [13] with the main components 27.65 vol% propane and 68.28 vol% butane and

$$v_{\text{burn}} = -177.43 \cdot \phi^3 + 340.77 \cdot \phi^2 - 123.66 \cdot \phi - 0.2297 \quad (0.5 < \phi < 1.4) \quad (2.12)$$

for natural gas [14].

In Eqs. (2.11) and (2.12) v_{burn} is the burning velocity in cm s^{-1} and $\phi = 1/\lambda = n_{\text{L,min}}/n_{\text{L}}$ the ratio of the molar stoichiometric requirement of air, $n_{\text{L,min}}$, and the available number of moles of air ($\phi = 1$, stoichiometric). This value is called “equivalence ratio” and is the reciprocal of the air-to-fuel ratio $\lambda = 1$.

Example 2.7 Determination of the burning velocities for petroleum gas and natural gas

Determine the burning velocity of petroleum gas and natural gas for different equivalence ratios in steps of 0.1.

Solution

Application of Eqs. Gl. (2.11) and (2.12) leads to the values of Table 2.10; they are shown in Fig. 2.5.

Table 2.10 Laminar burning velocities for petroleum gas and natural gas as a function of the mixing ratio ϕ

Material/ ϕ	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4
Petroleum gas			21.0	30.0	36.2	39.6	40.3	38.3	33.5	26.1
Natural gas	1.0	9.9	19.3	28.1	35.2	39.5	39.9	35.5	25.1	7.7

Fig. 2.5 Laminar burning velocities for petroleum gas and natural gas as a function of the equivalence ratio

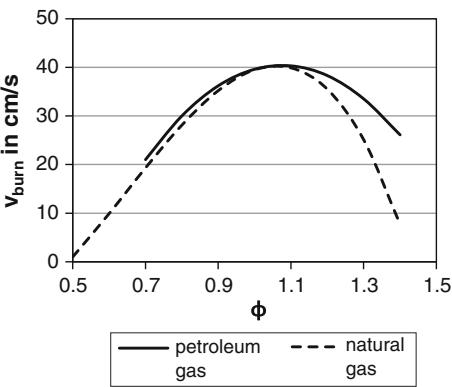


Table 2.11 Maximum experimental safe gaps (MESGs) for selected flammable materials (from [7])

Material	w_n in mm
Acetylene	0.37
Diethyl ether	0.87
1,2 Dichloroethane	1.80
Ethylene	0.65
Methane	1.14
Methanol	0.91
Propane	0.90
Carbon disulphide	0.34
Vinyl chloride	0.96
Hydrogen	0.29

2.1.1.6 Critical Slot Width and Maximum Experimental Safe Gap

Propagation of flames is hindered if they have to cross a small slot. This phenomenon is characterized by the critical slot width and the maximum experimental safe gap (MESG). According to [3] the critical slot width is the width of a slot with given length which after an explosion of the readily ignitable mixture or flammable vapour just prevents the ignition of the mixture on the other side of the slot. The critical slot “decouples” the space in which an explosion occurs from the surrounding flammable atmosphere. The MESG is the lowest value of the critical slot widths. It is measured by varying the composition of the mixture [7]. Details on the measuring process can be found in [3].

The most flammable concentration is found to lie between 0.9 and 1.4 respectively 0.8 and 2 times the stoichiometric concentration. The latter may be determined from Eq. (2.5). Table 2.11 provides MESGs for selected materials.

Example 2.8 Determination of most easily ignited concentrations

Determine the most easily ignited concentrations for the hydrocarbons from Table 2.8 and for hydrogen assuming that it occurs at 1.1 times the stoichiometric composition.

Solution

The calculations are based on Eqs. (2.3)–(2.5). The results are shown in Table 2.12.

Table 2.12 Assessment of the most easily ignited concentrations

Material	m	x	y	z according to Eq. (2.4)	$c_{st} \cdot 1.1$ in vol.% according to Eq. (2.5)
Acetylene	2	2	0	2.5	8.5
Diethyl ether	4	10	1	6	3.7
Ethylene	2	4	0	3	7.2
Methane	1	4	0	2	10.5
Methanol	1	4	1	1.5	13.5
Propane	3	8	0	5	4.4
Hydrogen	0	2	0	0.5	32.5

□

2.1.1.7 Basic Flame Types

After presenting several of the safety parameters of fire and explosion protection different types of flames are briefly discussed here. The presentation largely draws upon [15].

Basically we distinguish between pre-mixed or non pre-mixed (formerly called “diffusion flames”) flames. With pre-mixed flames the mixing between fuel and oxidant occurs before combustion with non pre-mixed flames mixing and combustion are simultaneous. A pre-mixed flame is obtained, for example, if the air supply of a Bunsen burner is opened; if it is closed the flame becomes non pre-mixed. Another example of a non pre-mixed flame is a burning candle.

Further differentiations are found in Fig. 2.6. In what follows they are briefly commented upon.

For pre-mixed flames the velocity of combustion is limited by the kinetics of the combustion process. In case of a laminar non pre-mixed flame the limitation usually stems from the diffusion velocity of air into the fuel, with turbulent non pre-mixed flames on the other hand the kinetics becomes more determining.

Laminar pre-mixed flame

The combustion velocity of a freely burning flat flame into the unburnt mixture can be described by the laminar burning velocity (vid. Sect. 2.1.1.5). In doing this different regimes of combustion can be distinguished on the basis of the equivalence ratio ϕ .

$\phi < 1$ lean (there is oxygen left after combustion)

$\phi = 1$ stoichiometric (only combustion products remain after the combustion)

$\phi > 1$ rich (fuel is left after the combustion)

If the velocity of the unburnt gas is smaller than the laminar burning velocity the flame flashes back into the outlet opening. In the opposite case blow-off occurs (slight separation from the outlet) and at even higher flow velocities the flame lifts.

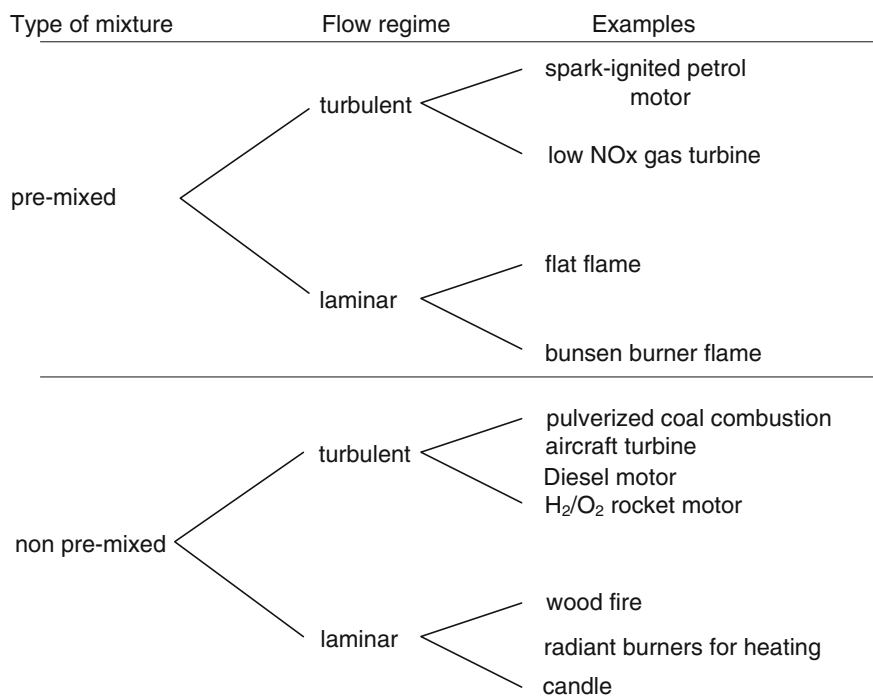


Fig. 2.6 Differentiation of flame types (according to [15])

Turbulent pre-mixed flame

The transition from laminar to turbulent flames occurs for $Re \approx 2,000$ with the Reynolds number referring to the flame. It is smaller than in the unburnt mixture because the viscosity of gases rises with increasing flame temperature. The combustion process of a turbulent pre-mixed flame can be controlled well. However, for safety reasons it is not readily applied because flammable mixtures may accumulate and hence explode.

Laminar non pre-mixed flame

Non pre-mixed flames are characterized by more complex chemical processes than pre-mixed ones and may comprise the entire spectrum $0 < \phi < \infty$. They occur if a pure fuel flows from an outlet opening and is then mixed with the surrounding air and thus with oxygen by diffusion and entrainment. Contrary to pre-mixed flames non pre-mixed flames do not propagate and hence cannot be characterized by the laminar burning velocity. For the flame length we have [16]

$$L \approx \frac{c_0}{c_{st}} \cdot \frac{\dot{V}}{4\pi D \left(1 + \frac{c_{st}}{2c_0}\right)} \quad (2.13)$$

and according to Jost (cit. in [5])

$$L \approx \frac{\dot{V}}{\pi D} \quad (2.14)$$

and according to [7]

$$L \approx \frac{\dot{V}}{2\pi D} \quad (2.15)$$

In Eqs. (2.13)–(2.15) L is the flame length in m, c_0 the concentration of the fuel at the outlet opening (fuel/air ratio: usually equal to 1, respectively 100 %), c_{st} is the corresponding stoichiometric concentration, \dot{V} the volumetric flow rate in m^3s^{-1} and D the diffusion coefficient in m^2s^{-1} .

The equations suggest that the flame length at constant mixture ratio only depends on the volumetric flow rate, i.e. it is independent of the cross section of the outlet opening. With a given outlet cross section it is approximately proportional to the flow velocity. The differences between the relationships point to modelling uncertainties.

Turbulent non-premixed flame

With increasing velocity at the outlet the laminar flame becomes turbulent. The transition between the two regimes occurs at $\text{Re} \approx 2,000$. Contrary to laminar non pre-mixed flames its length does not depend on the velocity at the outlet.

Example 2.9 Determination of the lengths of non pre-mixed flames

Determine the flame lengths of non pre-mixed laminar flames for the flammable gases hydrogen, carbon monoxide and acetylene at a volumetric flow of $0.0001 \text{ m}^3\text{s}^{-1}$.

Data: $D_{\text{H}_2} = 7.1 \times 10^{-5} \text{ m}^2\text{s}^{-1}$; $D_{\text{CO}} = 2.03 \times 10^{-5} \text{ m}^2\text{s}^{-1}$; $D_{\text{C}_2\text{H}_2} = 1.62 \times 10^{-5} \text{ m}^2\text{s}^{-1}$.

Solution

The bases are Eqs. (2.13) and (2.5) as well as Eqs. (2.14) and (2.15). The resulting flame lengths are contained in Table 2.13.

Table 2.13 Flame lengths for selected gases in m

Material	c_{st} in %	Equation (2.13)	Equation (2.14)	Equation (2.15)
Hydrogen	29.58	0.33	0.45	0.22
Carbon monoxide	29.58	1.15	1.57	0.78
Acetylene	7.75	6.12	1.96	0.98

2.1.1.8 Adiabatic Flame Temperature

The adiabatic flame temperature indicates the thermal power radiated by the flame. It represents an upper limit,

- because it is determined assuming combustion without losses and
- because often the ionization and dissociation of the combustion products, which start above 1,370 °C and consume energy thus reducing the temperature, are not accounted for [5].

The adiabatic flame temperature applies to pre-mixed flames, usually in stoichiometric mixtures with oxygen from air. Non pre-mixed flames reach temperatures of appr. 1,500 K. If the oxidant is pure oxygen instead of oxygen from the air the occurring temperatures are 700–800 K higher.

The first law of thermodynamics applies to an adiabatic system (heat losses $dq = 0$) at constant pressure [17]. Accordingly the sum of the enthalpies is equal to zero. Hence, we obtain for calculating the adiabatic flame temperature

$$\sum_{i=1}^I n_i \cdot \Delta h_{in,i} + \sum_{j=1}^J m_j \cdot \Delta h_{out,j} + \Delta H_c = 0 \quad (2.16)$$

In Eq. (2.16) n_i is the number of moles of input material number i with the corresponding difference of enthalpy between its temperature (normally ambient) and the standard temperature (298.15 K), $\Delta h_{in,i}$. It is equal to zero if its initial temperature equals the standard temperature, m_j is the number of moles of combustion product j and $\Delta h_{out,j}$ the corresponding difference in enthalpy between the initial temperature and the adiabatic flame temperature of the combustion products; ΔH_c is the enthalpy of combustion of the fuel in question. For ΔH_c the net calorific value of the fuel is used, i.e. $\Delta H_c = -C_n$.

The enthalpy at the standard pressure of 101.3 kPa and at a temperature of t in K/1,000, h^0 in kJ/mol, can be obtained from [18], where the following representation is used for a number of materials

$$h^0 - h_{298.15}^0 = A \cdot t + B \cdot \frac{t^2}{2} + C \cdot \frac{t^3}{3} + D \cdot \frac{t^4}{4} - \frac{E}{t} + F - H \quad (2.17)$$

In Eq. (2.17) $h_{298.15}^0$ is the standard enthalpy (at 101.3 kPa and 298.15 K), which cancels on forming the enthalpy differences in Eq. (2.16). The relationship between enthalpy and heat capacity at constant pressure is useful for practical applications

$$h^0 - h_{298.15}^0 = \int_{298.15}^T c_p(T) dT \quad (2.18)$$

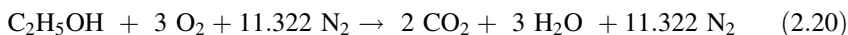
where $T = t \cdot 1,000$ is the temperature in K.

Table 2.14 contains coefficients for applying Eq. (2.17) and Table 2.15 experimentally and theoretically determined adiabatic flame temperatures for selected materials. The latter were calculated iteratively from Eq. (2.16). For this purpose the following reaction equations were used assuming air to consist of oxygen and nitrogen only so that 1 mol of oxygen is accompanied by 3.774 mol of N₂:

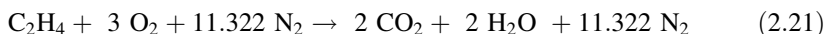
Acetylene



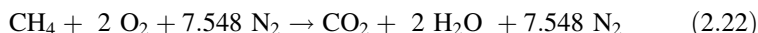
Ethanol



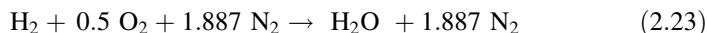
Ethylene



Methane



Hydrogen



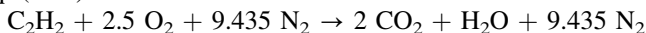
Example 2.10 Determination of the adiabatic flame temperature of acetylene

Determine the adiabatic flame temperature of acetylene for an initial temperature of 25 °C using the following mean values for the heat capacities at constant pressure. The net calorific value of acetylene, C_n, is taken from Table 2.15.

Data : c_{p,CO₂} = 49.6 J/(mol K); c_{p,H₂O} = 44.6 J/(mol K); c_{p,N₂} = 33.0 J/(mol K)

Solution

Based on Eq. (2.16) and accounting for Eq. (2.18) we obtain for the reaction Eq. (2.19)



the following enthalpy balance

$$0 = (T - 298.15) \cdot (2 \cdot 49.6 + 1 \cdot 44.6 + 9.435 \cdot 33.0) - 1,255,600$$

Solving this equation for T gives an adiabatic flame temperature of 3,056.8 K. □

Table 2.14 Coefficients for determining the enthalpy of selected materials (from [18])

Material	Temperature range in K	A	B	C	D	E	F	H
CO	298–1,300	25.56759	6.096130	4.054656	−2.671301	0.131021	−118.0089	−110.5271
	1,300–6,000	35.15070	1.300095	−0.205921	0.013550	−3.282780	−127.8375	−110.5271
CO ₂	298–1,200	24.99735	55.18696	−33.69137	7.948387	−0.136638	−403.6075	−393.5224
	1,200–6,000	58.16639	2.720074	−0.492289	0.038844	−6.447293	−425.9186	−393.5224
H ₂ O	500–1,700	30.09200	6.832514	6.793435	−2.534480	0.082139	−250.8810	−241.8264
	1,700–6,000	41.96426	8.622053	−1.499780	0.098119	−11.15764	−272.1797	−241.8264
O ₂	100–700	31.32234	−20.23531	57.86644	−36.50624	−0.007374	−8.903471	0.0
	700–2,000	30.03235	8.772972	−3.988133	0.788313	−0.007374	−11.32468	0.0
N ₂	2,000–6,000	20.91111	10.72071	−2.020498	0.146449	9.245722	5.337651	0.0
	100–500	28.98641	1.853978	−9.647459	16.63537	0.000117	−8.671914	0.0
H ₂	500–2,000	19.50583	19.88705	−8.598535	1.369784	0.527601	−4.935202	0.0
	2000–6,000	35.51872	1.128728	−0.196103	0.014662	−4.553760	−18.97091	0.0
CH ₄	298–1,000	33.066178	−11.363417	11.432816	−2.772874	−0.158558	−9.980797	0.0
	1,000–2,500	18.563083	12.257357	−2.859786	0.268238	1.977990	−1.147438	0.0
	2500–6,000	43.413560	−4.293079	1.272428	−0.096876	−20.533862	−38.515158	0.0
	298–1,300	−0.703029	108.4773	−42.52157	5.862788	0.678565	−76.84376	−74.87310
	1,300–6,000	85.81217	11.26467	−2.114146	0.138190	−26.42221	−153.5327	−74.87310

Table 2.15 Experimental and theoretical values of the adiabatic flame temperatures for selected materials (initial temperature 25 °C)

Material	Experimental in K		Theoretical in K	C _n in kJ/mol [17]
	a	b		
Acetylene		2,598	2,903	1,255.6
Ethanol			2,288	1,234.8
Ethylene	2,248	2,253	2,561	1,322.9
Methane	2,148	2,158	2,323	802.34
Hydrogen		2,318	2,520	241.82

^aSiegel and Howell (cited according to [5])^bLewis and von Elbe (cited according to [5])

2.1.1.9 Explosions

As already mentioned the ignition of a flammable material may cause a fire or an explosion. An explosion is understood to be the sudden and violent release of energy. The violence of the explosion then depends on the rate of energy release. For example, the energy stored in a car tyre causes an explosion if the tyre bursts. On the other hand it may be gradually dissipated through a puncture. The following types of energy may lead to an explosion:

- physical energy
 - pressure energy of gases
 - strain energy of metals
 - electrical energy
 - heat energy
 - quick phase change (steam explosion)
- chemical energy
 - combustion reactions
 - dust explosions
 - runaway reactions
 - decomposition
 - polymerization
 - explosives
- nuclear energy (uncontrolled chain reaction)

In what follows explosions caused by combustion reactions are treated first. Runaway reactions, decomposition and polymerization are a subject of Chap. 3, explosives are treated in Sect. 2.5 and explosions resulting from physical energy in Sects. 10.7 and 10.9. Nuclear explosions are outside the scope of this book.

Two types of explosions due to chemical energy are distinguished

- deflagration
and
- detonation.

In a deflagration the flammable mixture burns relatively slowly. Flame propagation is mainly determined by molecular diffusion and turbulent transport processes. Mixtures of hydrocarbons and air burn in the absence of turbulence, i.e. under laminar or almost laminar conditions, with flame speeds of the order of 5–30 m/s. If there is no confinement this is too slow to produce tangible overpressures and only a flash fire is produced. That is why there is always turbulence involved in a vapour cloud explosion (turbulent flame speeds 100–300 m/s), which increases the rate of combustion and hence the overpressure [12].

A detonation is totally different. The flame front moves as a pressure wave closely followed by a combustion wave, which supplies the energy nourishing the pressure wave. A stationary detonation pressure wave reaches the velocity of sound corresponding to the hot gases. This velocity lies well above that for unburnt gases. For hydrogen-air mixtures the velocity is of the order of 2,000–3,000 m/s compared with 300 m/s in air of 0 °C.

A detonation causes a stronger pressure wave and more destruction than a deflagration. Whilst the peak pressure of a deflagration produced by a mixture of hydrocarbons and air in a confined space amounts to about 8 bar, 15–20 bar are reached following a detonation. Contrary to a deflagration a detonation does not have to occur in a confined space in order to produce such high pressures [5].

A detonation is not a stable but a fluctuating process. This finds its expression in a cellular structure of shock and reaction waves. The cell structure depends on the type of fuel and the composition of the mixture. More reactive mixtures have smaller cell sizes. Hence, cell size is a measure for the propensity of a material to detonate (cf. Table 2.16). Table 2.16 shows as well that lower ignition energies are required for a deflagration, whilst the direct triggering of a detonation requires high energies [19]. The range of concentrations in which a detonation is possible is always smaller than that for ignition (UEL–LEL) (cf. [4]). However, it becomes broader with increasing initial pressures and temperatures.

A deflagration may turn into a detonation, especially if it propagates through a pipe. Such a process is called Deflagration-Detonation-Transition (DDT). Research has not yet totally clarified its characteristics (cf. [20, 21]).

Basically it may be stated that turbulence enhancing circumstances such as obstacles, building structures, and confinements as well as high ignition energies favour the transition from deflagration to detonation. The same is true for high initial pressures and temperatures.

Table 2.16 Characteristic detonation cell sizes and ignition energies for the deflagration and detonation of selected stoichiometric fuel-air mixtures (from [19])

Flammable material	Cell size in mm	Minimum ignition energy in mJ	
		Deflagration	Detonation
Methane	300	0.28	2.3×10^{11}
Propane	55	0.25	2.5×10^9
Propylene	55	0.28	7.6×10^8
Ethylene	25	0.07	1.2×10^8
Acetylene	10	0.007	1.29×10^5

One must differentiate as well between confined and unconfined explosions. Typical confinements are vessels and pipework as well as buildings. Unconfined explosions (outdoors) exhibit other characteristics than confined ones (vid. Sect. 10.6.3).

2.1.1.10 Maximum Pressure and Maximum Rate of Pressure Rise

Deflagration

The strength of an explosion is characterized by its maximum pressure and its maximum rate of pressure rise. The standardized methods for measuring these parameters are described in [22].

The maxima of the explosion parameters depend on the vessel volume. Whilst the maximum pressures of conventional fuels (flammable vapours) may generally be constant and only dependent on vessel volume the maximum rate of pressure rise may adopt very different values depending on the type of fuel and vessel volume.

The volume dependence of the maximum rate of pressure rise of a flammable gas or vapour can be described by the cube root law

$$\frac{dp}{dt}_{\max} \cdot V^{1/3} = K_G = \text{const.} \quad (2.24)$$

In Eq. (2.24) the unit of the vessel volume has to be compatible with that of K_G , i.e. m^3 for the K_G values from Table 2.17, which additionally also contains maximum pressures; dp/dt_{\max} then results in bar s^{-1} .

Table 2.17 Characteristic values for the explosion of flammable gases and vapours (5-l sphere for explosion tests, ignition energy $E = 10 \text{ mJ}$, standard conditions) from [3]

Flammable Material	p_{\max} in bar	K_G in bar m s^{-1}
Butane	8.0	92
Ethane ^a	7.8	106
Ethylbenzene ^a	7.4	96
Methane	7.1	55
Methyl alcohol ^a	7.5	75
Propane	7.9	100
Carbon disulphide	6.4	105
Hydrogen sulphide	7.4	45
Hydrogen	6.8	550

^aExtrapolated value

Example 2.11 Maximum rates of pressure rise for the deflagration of methane and hydrogen

Determine the maximum rates of pressure rise for vessel sizes between 5 l and 10 l in steps of 1 l for methane and hydrogen.

Solution

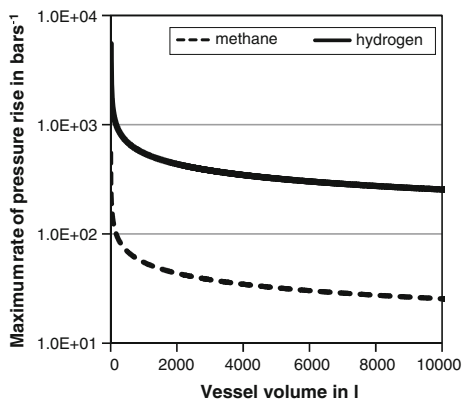
Using Eq. (2.24) in conjunction with Table 2.17 we obtain $\frac{dp}{dt}_{\max} = \frac{55}{V^{1/3}}$ for methane and $\frac{dp}{dt}_{\max} = \frac{550}{V^{1/3}}$ for hydrogen

The results for the maximum rates of pressure rise in bar s^{-1} are given in Table 2.18 and in Fig. 2.7 for an even larger range of volumes.

Table 2.18 Maximum rates of pressure rise for deflagrations of methane and hydrogen in bar s^{-1}

Flammable material	5 l	6 l	7 l	8 l	9 l	10 l
Methane	321.6	302.7	287.5	275.0	264.4	255.3
Hydrogen	3,216	3,027	2,875	2,750	2,644	2,553

Fig. 2.7 Maximum rates of pressure rise for methane and hydrogen as a function of vessel volume

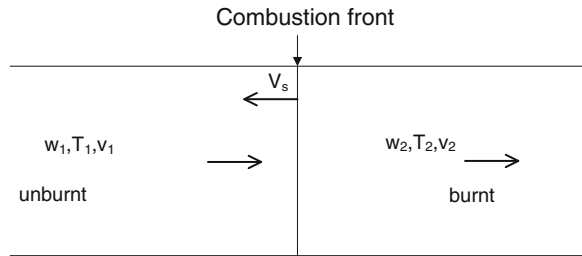


□

Detonation

A detonation is usually modelled as a one dimensional shock wave (vid. [5, 23, 24]). For this purpose a coordinate system is used which moves with the combustion front (velocity $V_s = -w_1$ in the coordinate system of an outside observer, also called laboratory system, vid. Figure 2.8). The following relations are used in the model in order to relate the state after the detonation (subscript 2) with that before the detonation (subscript 1):

Fig. 2.8 Schematic for deriving the equations governing a detonation



Conservation of mass flux

$$\frac{w_1}{v_1} = \frac{w_2}{v_2} \quad (2.25)$$

Conservation of momentum

$$p_1 + \frac{w_1^2}{v_1} = p_2 + \frac{w_2^2}{v_2} \quad (2.26)$$

Conservation of energy

$$h_2 + \frac{w_2^2}{2} - \left(h_1 + \frac{w_1^2}{2} \right) = C_n \quad (2.27)$$

Inserting Eqs. (2.25) and (2.26) in Eq. (2.27) we have

$$h_2 - h_1 - C_n = \frac{1}{2}(p_2 - p_1) \cdot (v_1 + v_2) \quad (2.28)$$

Additionally the ideal gas equation of state is invoked

$$p \cdot v = R \cdot T \quad (2.29)$$

Equation (2.28) establishes a relationship between pressure and specific volume (enthalpy is related via heat capacity and Eq. (2.29) with pressure and specific volume). It is called Hugoniot equation or Hugoniot shock adiabat and consists of thermodynamic quantities only.

The foregoing equations use the following nomenclature:

- w : velocity of gases relative to the combustion front in m/s
- p : pressure in Pa
- v : specific volume in kg/m³
- h : enthalpy in J/kg
- C_n : net calorific value (heat of reaction) in J/kg
- M : molar mass of the flammable gas

R_m : universal gas constant $R_m = 8.3145$ (J/mol K)

R : mass basis gas constant $R = R_m / M$ in J/(kg K)

The following relations apply

$$h_2 = \sum_{j=1}^J \frac{y_j}{M_j} \cdot \Delta h_{out,j} \quad \text{and} \quad h_1 = \sum_{i=1}^I \frac{y_i}{M_i} \cdot \Delta h_{in,i} \quad (2.30)$$

In Eq. (2.30) y denotes the molar fractions and M the molar masses.

From Eqs. (2.26) and (2.25) we obtain the velocity of the shock wave D

$$D = w_1 + V_1 = v_1 \cdot \left(\frac{p_2 - p_1}{v_1 - v_2} \right)^{\frac{1}{2}} \quad (2.31)$$

since V_1 , the velocity of the unburnt gas moving into the combustion front, is equal to zero.

A detonation is characterized by the rapid change of pressure accompanying the combustion process. This change is derived from Eqs. (2.26) and (2.25) giving

$$p_2 - p_1 = \left(\frac{w_1}{v_1} \right)^2 (v_2 - v_1) \quad (2.32)$$

Equation (2.32) connects the state before the combustion (1) with that after the combustion (2); it is called Rayleigh line. From Eq. (2.32) we have for its gradient

$$\frac{p_2 - p_1}{v_2 - v_1} = - \left(\frac{w_1}{v_1} \right)^2 = - \left(\frac{w_2}{v_2} \right)^2 \quad (2.33)$$

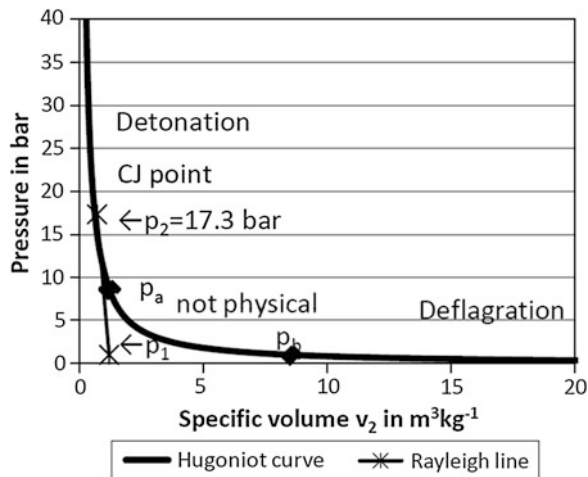
The solution for the detonation pressure has to satisfy Eqs. (2.28) and (2.33). This condition leads to an infinite number of solutions. According to Chapman and Jouguet one has to choose the one for which the Rayleigh line is a tangent to the Hugoniot curve (point CJ in Fig. 2.9). Entropy becomes a maximum at this point (vid. [23]).

Figure 2.9 shows the Hugoniot curve for the stoichiometric combustion of hydrogen. It is based on the evaluation of Eq. (2.28) and serves for some more general explanations.

The curve consists of three regions: explosions with pressures after combustion $p_2 > p_a$, which is characteristic of detonations, and $p_2 < p_b$, which means deflagration. In between there is a physically non permissible region, which is characterized by the fact that the corresponding pairs of values (v_2, p_2) lead to imaginary solutions for the velocities according to Eq. (2.31).

For $p_2 > p_a$ the combustion front moves with supersonic velocity and for $p_2 < p_b$ with subsonic velocity. The differentiation has to be based on the velocity

Fig. 2.9 Hugoniot curve and Rayleigh line between (p_1, v_1) and (p_2, v_2) for the stoichiometric combustion of hydrogen (CJ-Chapman-Jouguet point with the corresponding pressure $p_2 = p_{CJ}$)



of sound applicable to the pertinent temperature T_2 and gas composition, which is obtained from

$$c_2 = \sqrt{\kappa_2 \cdot p_2 \cdot v_2} = \sqrt{\kappa_2 \cdot R_2 \cdot T_2} \quad (2.34)$$

In Eq. (2.34) R_2 is the mass basis gas constant for the gas mixture after the combustion in $J/(kg \cdot K)$ and κ_2 the corresponding heat capacity ratio.

Example 2.12 Simplified determination of detonation pressure and velocity for hydrogen

Determine the detonation pressure and the corresponding velocity for hydrogen. The initial pressure for the detonation is $p_1 = 1$ bar and the initial temperature $T_1 = 298.15$ K.

Data:

Mean values for the heat capacities: $c_{p,H_2O} = 44.6$ J/(mol K); $c_{p,N_2} = 33.0$ J/(mol K)

Molar masses: hydrogen $M_{H_2} = 2.016$ g/mol, oxygen $M_{O_2} = 31.998$ g/mol, nitrogen $M_{N_2} = 28.013$ g/mol, steam $M_{H_2O} = 18.015$ g/mol.

Solution

According to Zeldovich (vid. [5]) the detonation pressure p_2 may be approximated by

$$p_2 \approx 2 \cdot p_v \quad (2.35)$$

where p_v is the pressure after an isochoric combustion. Because of

$$c_v = c_p - R$$

we obtain

$$c_{v,H_2O} = 44.6 \text{ J}/(\text{mol K}) - 8.3145 \text{ J}/(\text{mol K}) = 36.29 \text{ J}/(\text{mol K})$$

$$c_{v,N_2} = 33.0 \text{ J}/(\text{mol K}) - 8.3145 \text{ J}/(\text{mol K}) = 24.69 \text{ J}/(\text{mol K})$$

By using the reaction Eq. (2.23) and C_n from Table 2.15 for the isochoric heat-up we arrive at

$$(T_2 - T_1) \cdot (n_{H_2O} \cdot c_{v,H_2O} + n_{N_2} \cdot c_{v,N_2}) = C_n \quad (2.36)$$

Solving Eq. (2.36) for the temperature T_2 gives

$$\begin{aligned} T_2 &= \frac{H_u}{n_{H_2O} \cdot c_{v,H_2O} + n_{N_2} \cdot c_{v,N_2}} \\ &+ T_1 = \frac{241,820 \frac{\text{J}}{\text{mol}}}{1 \text{ mol} \cdot 36.29 \frac{\text{J}}{\text{mol K}} + 1.887 \text{ mol} \cdot 24.69 \frac{\text{J}}{\text{mol K}}} \\ &+ 298.15 \text{ K} = 3,215.9 \text{ K} \end{aligned}$$

The corresponding pressure is

$$p_v = p_1 \cdot \left(\frac{T_2}{T_1} \right) = 100,000 \frac{\text{kg m}}{\text{m}^2 \text{s}^2} \cdot \left(\frac{3215.9 \text{ K}}{298.15 \text{ K}} \right) = 10786181.5 \frac{\text{kg m}}{\text{m}^2 \text{s}^2}$$

According to Eq. (2.35) the pressure of the shock wave is

$$p_2 \approx 2 \cdot 10786181.5 \frac{\text{kg m}}{\text{m}^2 \text{s}^2} = 21572363 \frac{\text{kg m}}{\text{m}^2 \text{s}^2} \approx 21.6 \text{ bar}$$

Using the ideal gas equation of state Eq. (2.31) provides the corresponding detonation velocity

$$D = w_1 + V_1 = v_1 \cdot \left(\frac{p_2 - p_1}{v_1 - v_2} \right)^{\frac{1}{2}}$$

where

$$v_1 = \frac{R_m \cdot T_1}{p_1 \cdot M_{\text{reactants}}} \quad \text{and} \quad v_2 = \frac{R_m \cdot T_2}{p_2 \cdot M_{\text{products}}}$$

From Eq. (2.23) we obtain with $n_{\text{reactants}} = n_{H_2} + n_{O_2} + n_{N_2} = 1 + 0.5 + 1.887 = 3.387$ the following molar mass for the mixture of reactants

$$\begin{aligned}
M_{\text{reactants}} &= \frac{n_{\text{H}_2}}{n_{\text{reactants}}} \cdot M_{\text{H}_2} + \frac{n_{\text{O}_2}}{n_{\text{reactants}}} \cdot M_{\text{O}_2} + \frac{n_{\text{N}_2}}{n_{\text{reactants}}} \cdot M_{\text{N}_2} \\
&= 0.2952 \cdot 2.016 \frac{\text{g}}{\text{mol}} + 0.1476 \cdot 31.998 \frac{\text{g}}{\text{mol}} + 0.5571 \cdot 28.013 \frac{\text{g}}{\text{mol}} = 20.930 \frac{\text{kg}}{\text{kmol}}
\end{aligned}$$

and for the mixture of reaction products with $n_{\text{products}} = n_{\text{H}_2\text{O}} + n_{\text{N}_2} = 1 + 1.887 = 2.887$

$$\begin{aligned}
M_{\text{products}} &= \frac{n_{\text{H}_2\text{O}}}{n_{\text{products}}} \cdot M_{\text{H}_2\text{O}} + \frac{n_{\text{N}_2}}{n_{\text{products}}} \cdot M_{\text{N}_2} \\
&= 0.3464 \cdot 18.015 \frac{\text{g}}{\text{mol}} + 0.6536 \cdot 28.013 \frac{\text{g}}{\text{mol}} = 24.5497 \frac{\text{kg}}{\text{kmol}}
\end{aligned}$$

Hence, we obtain the velocity of the shock wave as

$$\begin{aligned}
D &= \frac{R_m \cdot T_1}{p_1 \cdot M_{\text{reactants}}} \cdot \left(\frac{p_2 - p_1}{\frac{R_m \cdot T_1}{p_1 \cdot M_{\text{reactants}}} - \frac{R_m \cdot T_2}{p_2 \cdot M_{\text{products}}}} \right)^{\frac{1}{2}} = \frac{8314.5 \frac{\text{J}}{\text{kmol K}} \cdot 298.15 \text{ K}}{100000 \frac{\text{kg m}}{\text{m}^2 \text{s}^2} \cdot 20.93 \frac{\text{kg}}{\text{kmol}}} \\
&\cdot \left(\frac{\frac{21572363 \frac{\text{kg m}}{\text{m}^2 \text{s}^2} - 100000 \frac{\text{kg m}}{\text{m}^2 \text{s}^2}}{\frac{8314.5 \frac{\text{J}}{\text{kmol K}} \cdot 298.15 \text{ K}}{100000 \frac{\text{kg m}}{\text{m}^2 \text{s}^2} \cdot 20.93 \frac{\text{kg}}{\text{kmol}}} - \frac{8314.5 \frac{\text{J}}{\text{kmol K}} \cdot 3215.9 \text{ K}}{21572363 \frac{\text{kg m}}{\text{m}^2 \text{s}^2} \cdot 24.5497 \frac{\text{kg}}{\text{kmol}}}} \right)^{\frac{1}{2}} = 5154.1 \frac{\text{m}}{\text{s}}
\end{aligned}$$

However, the result lies considerably above the value to be expected from Table 2.19. \square

Example 2.13 Numerical calculation of the detonation pressure for selected reactions

Determine the detonation velocities and pressures for the following flammable gases: methane (CH_4), hydrogen (H_2), ethylene (C_2H_4), acetylene (C_2H_2) in air and acetylene with 2.5 mol of oxygen.

Solution

The calculation is performed using Eqs. (2.28) and (2.33). The enthalpies are determined on the basis of Eq. (2.17) in conjunction with Table 2.14. Rearranging Eq. (2.28) we have

$$h_2 - h_1 - C_n - \frac{1}{2}(p_2 - p_1) \cdot (v_1 + v_2) = 0$$

Invoking the ideal gas equation of state the value of T_2 satisfying the above equation for an assumed value of p_2 is determined via bisection (vid. [25]). This

gives a value for v_2 , too. Stepwise modification of p_2 and a renewed search for T_2 enables one to calculate the Hugoniot curve (cf. Fig. 2.9).

The gradient of the Hugoniot curve may now be approximated by the quotient of differences

$$\frac{p_2^i - p_2^{i-1}}{v_2^i - v_2^{i-1}}$$

The superscript i refers to the present value of p_2 , the superscript $i-1$ to the preceding one; the analogue applies to v_2 . The calculation was performed for $p_2^i - p_2^{i-1} = 30 \text{ kgm}/(\text{m}^2\text{s}^2)$, a step width which proved adequate.

The gradient of the Rayleigh line is (vid. Gl. (2.33))

$$\frac{p_2^i - p_1}{v_2^i - v_1}$$

By setting both gradients equal to each other the Chapman-Jouguet point is found. In doing this one requires that the modulus of the relative deviation of both values for the gradient is smaller than a predetermined upper limit ε , i.e.

$$\left| \frac{\frac{p_2^i - p_2^{i-1}}{v_2^i - v_2^{i-1}} - \frac{p_2^i - p_1}{v_2^i - v_1}}{\frac{p_2^i - p_1}{v_2^i - v_1}} \right| < \varepsilon$$

where ε is a small number, e.g. 10^{-5} . Table 2.19 contains the results. Mathematically more sophisticated procedures for finding the Chapman-Jouguet point are described in [23] and [24].

The differences between the calculated values and those from the literature are probably due to the more recent material parameters used and to accounting for the change in the number of moles caused by the reaction.

Table 2.19 Detonation pressures and velocities for selected reactions (final state: thermodynamic equilibrium)

Reaction	Pressure p_2 in bar	Pressure p_2 in bar (calculated)	Detonation velocity w_1 in m/s	Detonation velocity w_1 in m/s (calculated)
CH ₄ + air	17.4 [26]	18.5	1,803 [26]	1,901
H ₂ + air	15.8 cit. in [27]	17.3	1,968 cit. in [27]	1,997
C ₂ H ₄ + air	18.2 cit. in [27]	20.4	1,822 cit. in [27]	1,962
C ₂ H ₂ + air		24.5		2,038
C ₂ H ₂ + 2.5 O ₂		34.0		2,341

2.2 Chemically Unstable Materials: Decomposition and Polymerization

Decomposition and polymerization of materials which release energy are considered as hazardous; they are treated following [28]. The groups of materials with propensity to decomposition at ambient temperature are

- organic peroxides and
- self-reactive materials.

Materials are called self-reactive, if they have a propensity to violent exothermic decomposition at temperatures above ambient or by contact with impurities. These are mostly materials with sensitive nitrogen-nitrogen groups in the molecule.

Organic peroxides are materials which contain the bivalent peroxy-(O–O-) structural element and may be regarded as derivatives of hydrogen peroxides with one or both hydrogen atoms replaced by organic rests. They can already decompose exothermically at ambient temperature. The decomposition may be caused by heat, contact with impurities (e.g. acids and heavy metal compounds), friction or impact.

Whilst materials decompose by breaking up into smaller entities, the uncontrolled polymerization leads to the formation of large molecules, the polymers, and to a temperature rise if the heat of reaction is not removed sufficiently. The rate of heat removal decreases the larger the molecules become during the progressing polymerization. Table 2.20 provides an overview of the quantities of heat released by the aforementioned reactions, which by the way can also act as sources of ignition.

2.3 Flammable Liquids

Flammable liquids are classified in [29]. The properties of the liquids which form the basis for classification are given in Table 2.21.

The parameters flash point and fire point are used for characterizing flammable liquids.

2.3.1 Flash Point

The flash point of a liquid is the lowest temperature in °C corrected to 101.3 kPa of a flammable liquid in an open or closed cup at which vapours develop in such a quantity that under defined measuring conditions in the cup a vapour-air mixture is

Table 2.20 Heats of decomposition and polymerization of selected unstable materials (after [28])

Material	
<i>Peroxides</i>	<i>Heat of decomposition in kJ/mol</i>
Alkyl hydroperoxide	≈ 180
Dialkyl peroxide	170–180
Peroxydicarboxylic acids	80–90
Diacyl peroxide	120–130
<i>Self-reactive materials</i>	
Azobenzene	145.8
Azodicarbonamide	49.9
4-Nitrosophenol	147.7
Phenyldiazonium chloride	210.9
<i>Polymerizing materials</i>	<i>Heat of polymerization in kJ/mol</i>
Acrylic acid	67
Ethyl acrylate	80
Methyl acrylate	80
Methacrylic acid	42
Methyl methacrylate	59
Styrene	71
Vinyl acetate	88

Table 2.21 Classification of flammable liquids [29]

Characteristic	Flammable liquid		
	Category 1	Category 2	Category 3
Flash point	<23 °C	<23 °C	≥23 °C and ≤60 °C ^a
Initial boiling point	≤35 °C	>35 °C	
Hazard statement	H 224 extremely flammable liquid and vapour	H 225 highly flammable liquid and vapour	H 226 flammable liquid and vapour
Signal word	Danger	Danger	Warning
Past hazard class according to VbF	AI and B	AI and B	AII

^aFor the purpose of this regulation ([29]) gas oil, Diesel fuel and heating oils with a flashpoint between 55 and 75 °C may be considered as belonging to category 3

formed above the liquid surface which is just ignitable by an igniter from the outside [6]. There are several measuring methods (vid. [30]). Table 2.22 gives values for selected liquids.

Table 2.22 Characteristic parameters for flammable liquids (after [7])

Flammable liquid	Flash point in °C (closed cup)	Boiling point in °C	Categorization
Styrene	31	145	H 226
Chlorobenzene	28	132	H 226
Ethyl alcohol	12	78	H 225
Methanol	11	65	H 225
Petrol	< -20	60	H 224
Diethyl ether	< -20	35	H 224
Diesel fuel	>55	>155	may be assigned to H224 (cf. Table 2.21)

2.3.2 Fire Point

The fire point can provide information on fire hazards, for example after the spill of a flammable liquid, whilst the flash point indicates the existence of an explosive atmosphere.

The flash point implies that the ignited vapour goes out shortly after ignition, whereas the fire point is obtained by heating the liquid such that the fire continues after ignition (vid. [3]). Table 2.23 shows a comparison between the flash points and the fire points of selected materials.

2.4 Dusts

Materials which are flammable in solid state can explode if they are present as dusts, i.e. in the form of fine particles which can be whirled up and mixed with air. Then they behave similarly to exploding gases. Their propensity to explode is influenced by a number of factors. In [5] the following are named:

- chemical composition;
- particle size;
- moisture content;
- oxygen concentration;
- inert gas;
- admixed inert dust concentration.

Safety parameters are used to describe the combustion behaviour; they characterize the behaviour of

- deposited dust and
- dust dispersed in air

Table 2.23 Comparison of flash points and fire points (from [3])

Liquid	Boiling temperature in °C	Flash point in °C (closed cup)	Flash point in °C (open cup)	Fire point in °C
Toluene	110	6	14	18
Ethylene glycol	135	43	62	62
2-Butoxyethylacetate	192	88	98	98
Hexadecane	280	135	142	152

In what follows a few safety parameters are discussed; a detailed treatment including the measuring apparatuses is given in [3].

2.4.1 Self-Ignition

Flammable dusts already show a tendency to self-ignition at relatively low ambient temperatures, since a slow reaction with the oxygen of the air on the particle surfaces produces heat even at ambient temperature. Whether the final temperature reached lies below or above the self-ignition temperature (characterized by the equilibrium between heat production and removal) depends on the ratio of heat removal to the environment and heat production. The final temperature rises if the environmental temperature is increased, for example in an oven. The temperature at which the heat production is just larger than its removal is called self-ignition temperature. Apart from the properties of the material this temperature depends on the geometry of the bulk powder, which influences heat removal. More details on the theory of self-heating and self-ignition are found in Sect. 4.5.1.1.

2.4.2 Glow Temperature

The glow temperature is the lowest temperature, for which a dust layer with a thickness of 5 mm is ignited. It is determined under well-defined testing conditions on a hot plate (vid. [31]). The glow temperature decreases with increasing layer thickness. Additionally, grain size and bulk powder density influence the heat balance and hence the glow temperature. Table 2.24 contains values for selected materials.

2.4.3 Explosion Limits

Dust-air mixtures are flammable only within a certain range of concentrations just like gas-air mixtures. This range is marked by the lower explosion limit (LEL) and the upper explosion limit (UEL).

Table 2.24 Glow temperatures for selected materials [32]

Material	Maximum particle size in μm	Main particle size in μm	Bulk powder density in kg/l	Glow temperature in $^{\circ}\text{C}$
Phosphorus (red)	150	30–50	0.99	305
Iron powder	500	100–150	1.6	240
Rye flour	200	30–50	0.31	325
Wood dust (beech)	150	70–100	0.22	315
Charcoal	20	1–2	0.36	340
Naphthalene	300	80–100	0.53	Melts
Polyvinyl chloride	10	4–5	0.55	Carbonizes

The lower limit is of special practical interest. For many technical dusts it lies between 15 and 60 g/m^3 ; the UEL is very high, viz. 2–6 kg/m^3 . Investigations have shown that the LEL is largely independent of the ignition energy employed [3].

The temperature dependence of the LEL is described by [3]

$$\text{LEL}(T) = \text{LEL}(T_0) \cdot [1 - 0.0027 \cdot (T - T_0)] \quad (2.37)$$

In Eq. (2.37) $\text{LEL}(T)$ is the lower explosion limit at temperature T and $\text{LEL}(T_0)$ that at the reference temperature T_0 . Table 2.25 gives values for selected materials.

2.4.4 Minimum Ignition Energy

The minimum ignition energy (MIE) is the smallest quantity of energy stored in a capacitor which is sufficient to ignite the most flammable mixture of dust and air. The test is carried out under standardized conditions (vid. [33]). Table 2.26 gives values for selected materials.

Materials are categorized according to their minimum ignition energy

$\text{MIE} \geq 10 \text{ mJ}$: normally sensitive to ignition

$3 \text{ mJ} \leq \text{MIE} \leq 10 \text{ mJ}$: especially sensitive to ignition

$\text{MIE} \leq 3 \text{ mJ}$: extremely sensitive to ignition

Table 2.25 Lower explosion limits for selected materials and the ratio UEL/LEL at standard conditions [11]

Type of dust	LEL in gm^{-3}	UEL/LEL
Aluminum	35	172
Magnesium	25	223
Zirconium	45	544
Lignite	35	20

Table 2.26 Particle size and minimum ignition energy (MIE) for selected dusts [3]

Type of dust	Particle size in μm	MIE in mJ
Activated carbon	<10	500×10^3
Chicory	40	100
Pea flour, green	27	100
Sewage sludge (76 % organic)	89	50
Wax	<20	5
Lycopodium	32	2
Aluminum	<10	≈ 0.1

2.4.5 Limiting Oxygen Concentration (LOC)

The limiting oxygen concentration (LOC) is the maximum oxygen concentration of a flammable dust with air and an inert gas for which there is no self-sustaining propagation of flames for any fuel concentration. Fuel concentration is varied by varying the concentration of inert gas. The determination takes place under standardized test conditions (vid. [34]).

The oxidizing medium usually is air; yet substances like chlorine may serve as well. Oxygen concentrations higher than that of air (21 vol%) raise the combustion velocity and ignitability. The converse is also true. This offers possibilities for preventing dust explosions by reducing the O_2 contents by mixing with an inert material. In industry carbon dioxide, nitrogen, noble gases or inert dusts like calcium carbonate (CaCO_3) are used for this purpose [35]. Table 2.27 gives details.

Table 2.27 Limiting oxygen concentrations for inserting dust clouds in an O_2/N_2 atmosphere [35]

Dust type	Median of the particle diameter in μm	Maximum O_2 concentration on inerting with N_2 in vol%
Aluminum	22	5
Soot	<10	12
Charcoal	42	12
Wood	27	10
Cornstarch	17	9
Organic pigments	<10	12
Herbicides	10	12

2.4.6 Maximum Pressure and Maximum Rate of Pressure Rise

The maximum pressure, p_{\max} , and the maximum rate of pressure rise, $(dp/dt)_{\max}$, in closed vessels, frequently spherical ones with volumes of 20 l or 1 m³, characterize the strength of a dust explosion. The maximum strength is determined in a series of experiments by systematically varying the concentration of dust. The value may differ for the two vessel sizes. It was found that for vessels larger than 1 m³ the maximum explosion pressure virtually does not change. However, the maximum rate of pressure rise varies, as for flammable gases (cf. Sect. 2.1.1.10), according to

$$\frac{dp}{dt_{\max}} \cdot V^{1/3} = K_{st} = \text{const.} \quad (2.38)$$

Hence, the maximum rate of pressure rise decreases with increasing vessel volume. The pertinent measuring procedures are standardized in [36] and [37]. Table 2.28 shows values for selected dust-air mixtures.

Based on the value of K_{st} dusts are categorized in classes [38]. These classes serve to support the design of constructive protection measures for equipment. They are shown in Table 2.29.

Table 2.28 Maximum explosion pressures and K_{st} for selected dusts [3]

Type of dust	Particle size in μm	p_{\max} in bar	K_{st} in bar ms^{-1}
Activated carbon	<10	7.3	72
Chicory	40	8.5	157
Pea flour, green	27	9.1	109
Sewage sludge (76 % organic)	89	7.5	71
Wax	<20	8.4	185
Lycopodium	32	7.0	134
Aluminum	<10	11.4	625

Table 2.29 Categorization of dusts in explosion classes according to the value of K_{st}

K_{st} in bar ms^{-1}	Dust explosion class
0	0
0–200	1
200–300	2
>300	3

Example 2.14 Determination of the maximum rate of pressure rise of dust explosions

The maximum rate of pressure rise of dust explosions of sewage sludge and aluminum are to be compared for vessel volumes between 1 and 20 m³.

Solution

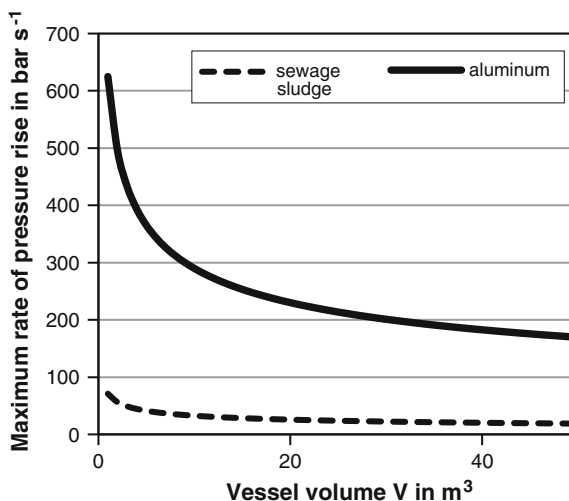
Using Eq. (2.38) and Table 2.28 we obtain $\frac{dp}{dt}_{\max} = \frac{71}{V^{1/3}}$ for sewage sludge and for aluminum $\frac{dp}{dt}_{\max} = \frac{625}{V^{1/3}}$

Table 2.30 shows the results for varying vessel volumes and Fig. 2.10 provides the corresponding graphical representation.

Table 2.30 Maximum rate of pressure rise for explosions of sewage sludge and aluminum dusts as a function of vessel volume

V in m ³	(dp/dt) _{max} in bar s ⁻¹ · sewage sludge	(dp/dt) _{max} in bar·s ⁻¹ aluminum
1	71	625
2	56.35	496.06
3	49.23	433.35
4	44.72	393.73
5	41.52	365.5
6	39.07	343.95
7	37.12	326.73
8	35.5	312.5
9	34.13	300.47
10	32.96	290.1
11	31.93	281.03
12	31.01	273
13	30.2	265.8
14	29.46	259.3
15	28.79	253.43
16	28.18	248.03
17	27.62	243.07
18	27.09	238.48
19	26.61	234.22
20	26.16	230.25

Fig. 2.10 Maximum rate of pressure rise for dust explosions as a function of vessel volume



2.5 Explosives

A material capable of an exothermic reaction such that gases and vapours are generated and released so rapidly that they cause destruction in their surroundings is called explosive. An explosion can occur only if the material has a big positive energy of formation or a large negative energy of decomposition. Such materials have a certain chemical structure. Since they are organic and mostly have reactive groups with available oxygen an intermolecular oxidation of their flammable part may occur. Examples for oxidizing reactive groups are nitro-, nitroso- and peroxy groups. Organic compounds containing acidic, acetylene or diazonium groups can also be strong explosives. Furthermore explosive mixtures can be produced by mixing inorganic oxidizing substances with flammable materials. Well known examples are: mixtures of potassium nitrate, sulphur and charcoal (black powder), of ammonium nitrate and fuel oil (ANFO) as well as nitrating mixtures containing potassium nitrate and oxidizing substances with hydrogen peroxide [39]. In [40] instructions are given for identifying materials which may potentially be explosive because they contain reactive groups. Explosible materials are categorized according to intended use and the type of handling hazard.

If the energy contents of a material is such that an explosion, the initiation of an explosion (by a small impact or a weak spark), a propellant (characterized by slow combustion) or a pyrotechnic effect can occur we are dealing with an explosive [40].

The characteristic of explosives is that they contain the oxygen required for combustion. Hence, they do not need an oxygen supply from outside and can therefore ignite even under water.

Explosives are characterized by a number of parameters [41], among them

- energy of formation;
- enthalpy of formation;
- brisance or shattering power;
- explosion energy;
- loading density;
- oxygen balance;
- nitrogen content;
- volume of explosion gases;
- thermal sensitivity;
- impact sensitivity;
- friction sensitivity;
- thermal stability.

Some of them are described below largely following [41]

2.5.1 Brisance

Brisance is the destructive fragmentation effect of a charge on its immediate vicinity. The relevant parameters are the detonation rate and the loading density (compactness) of the explosive, as well as the gas yield and the heat of explosion. Brisance is a measure for the time required to build up the maximum explosion pressure.

2.5.2 Loading Density

Loading density is understood to be the ratio between the mass of explosive and the volume available for the detonation. It depends on the production process, e.g. casting or pressing.

2.5.3 Oxygen Balance

The oxygen balance is the quantity of oxygen, expressed in percent mass, released by complete conversion of the explosive. If all the oxygen bonded in the explosive is not sufficient to convert the explosible material completely, the oxygen balance is negative. In the converse case it is positive (cf. Table 2.31).

2.5.4 Maximum Pressure

The blast wave produced by an explosion is caused by two mechanisms, the heating of the reaction products and the change in mole number. If an explosion progresses so fast that the volume at first remains unchanged and we deal with ideal gases the maximum pressure, p_s , is obtained as follows [42]

Table 2.31 Characteristics of selected explosives [41]

Substance	Molar mass in g	Chemical formula	Loading density in g/cm ³	Oxygen balance in %	Detonation velocity v_D in m/s ^a
Trinitrotoluene (TNT)	227.1	$C_7H_5N_3O_6$	0.82–1.07	−74	6,900 for $\rho = 1.6 \text{ g/cm}^3$
Ammonium-nitrate	80.0	NH_4NO_3	0.82–1.6 ^b	+20	–
Hexogen (cyclonite)	222.1	$C_3H_6N_6O_6$		−21.6	8,750 for $\rho = 1.76 \text{ g/cm}^3$
Trinitrobenzene	213.1	$C_6H_3N_3O_6$		−56.3	7,300 for $\rho = 1.71 \text{ g/cm}^3$
Nitroglycerin	227.1	$C_3H_5N_3O_9$		+3.5	7,600 for $\rho = 1.59 \text{ g/cm}^3$

^aThis is the detonation velocity under confinement (e.g. in a drilling hole) contrary to the detonation velocity in the open

^bDepending on the mixture, e.g. with TNT

$$p_s = \frac{p_a \cdot n_e \cdot T_e}{n_a \cdot T_a} \quad (2.39)$$

In Eq. (2.39) p is the pressure in Pa or bar, T the temperature in K, n the number of moles; the subscript “a” refers to the state before the explosion and “e” to that afterwards.

According to [43] the maximum pressure may also be obtained from

$$p_s = 9.9792 \cdot 10^{-10} \cdot \rho \cdot v_D^2 \quad (2.40)$$

In Eq. (2.40) ρ is the density in kg/m³ and v_D the detonation velocity in m/s (vid. Table 2.31). The maximum pressure, p_s , then results in bar.

2.5.5 Explosion Energy

The amount of energy released in an explosion depends on the initial and final states of the reaction. Yet it is difficult to determine the final state because the hot reaction products still undergo reactions during cooling. Explosives with a positive oxygen balance (rich in oxygen) will produce CO₂ and H₂O after the reaction; in case of a negative oxygen balance CO and H₂ will be encountered.

The following quantities are of interest:

- heat of combustion;
- energy of explosion;
- heat of explosion.

The heat of explosion is equal to the difference of the internal energies before and after the explosion, ΔU . The heat of combustion is the difference of the internal energies in case of stoichiometric combustion. The explosion energy equals the work done by the expansion of the gases, i.e.

$$w = - \int_1^2 p dV \quad (2.41)$$

In Eq. (2.41) 1 denotes the state before the explosion and 2 that afterwards. The sign is negative, if work is transferred out of the system boundaries and positive if it is introduced into the system; p is the pressure and V the volume.

The evaluation of the integral requires one to know the changes of pressure and volume during the explosion. Therefore it is difficult to be evaluated. It is easier to relate the thermodynamic states before and after the reaction with each other. This is achieved with the help of Helmholtz's free energy f . We have (cf. [5])

$$du = dw + dq \quad (2.42)$$

and using the relationship between heat and entropy $dq = Tds$

$$du = dw + Tds \quad (2.43)$$

Helmholtz's free energy is defined as

$$f = u - Ts \quad (2.44)$$

whence one obtains

$$df = du - Tds - sdT \quad (2.45)$$

In an isothermal process ($dT = 0$) the entire energy change is transformed into work. This gives

$$df = du - Tds \quad (2.46)$$

Inserting Eq. (2.43) in Eq. (2.46) we obtain

$$df = dw \quad (2.47)$$

Helmholtz's energy represents the maximum amount of work which a system can exert on its surroundings. Hence, it constitutes an upper bound for the work done by the explosion. Helmholtz's free energy is not normally found in tables. Therefore calculations based on Eq. (2.46) make use of the internal energy and entropy differences. We then have

$$du \approx \Delta u = (\Delta u_f^0)_P - (\Delta u_f^0)_R \quad (2.48)$$

which is the difference between the internal energies of formation of the reaction products $(\Delta u_f^0)_P$ and of the reactants $(\Delta u_f^0)_R$ at standard conditions, and

$$ds \approx \Delta s = s_P - s_R \quad (2.49)$$

which is the difference of the corresponding entropies. For the entropy we have

$$s = s^0 - R \cdot \sum_{(i)} n_i \cdot \ln \frac{n_i}{n} \quad (2.50)$$

In Eq. (2.50) s^0 is the entropy at standard conditions, n_i is the number of moles of the substance i and n the total number of moles. Since important contributions to the entropy are only made by the gaseous reaction products, the pressures $p_i = n_i/n$ are the partial pressures of product i in the mixture. The sum term in Eq. (2.50) constitutes the entropy increase caused by the irreversible mixing process (vid. [5]). Obviously it is only relevant if the mole numbers before and after the reaction differ substantially.

Application of the above considerations to the detonation of TNT leads to the following result (vid. [5])



In the first place the differences of the internal energies are formed. The necessary information is given in Table 2.32

Table 2.32 Thermodynamic properties of selected substances [6]

Substance	ΔU_f^0 in kJ/mol	ΔH_f^0 in kJ/mol	s^0 in kJ/(mol K)	ΔH_c^0 kJ/mol
C	0	0	0.00574	–
CO	–111.9 ^a	–110.53	0.197556	–283
CO ₂	–393.8 ^a	–393.51	0.213667	–
H ₂ O	–240.8 ^a	–241.814	0.188724	–
H ₂	0	0	0.130571	–241.82
N ₂	0	0	0.1915	–
O ₂	0	0	0.205043	–
Acetylene		228.2	0.20081	–1257
Ethylene	49.86 ^b	52.51	0.2192	–1323
TNT	–49.74 ^a	67.07*	0.27	–3295.9
Nitroglycerin	–349.71 ^a	–370.83*		–1529 ^c

^aFrom [41]; ^bcalculated; ^cfrom [18]

Table 2.33 Characteristics of selected explosives (from [41]), values behind the oblique bar from ([44])

Substance	Molar mass in g	Chemical formula	Explosion energy in kJ/kg (H ₂ O _{liq.})	Explosion energy in kJ/mol (H ₂ O _{liq.})
Trinitrotoluene (TNT)	227.1	C ₇ H ₅ N ₃ O ₆	4,564/4,520	1,036.5/1,026.5
Ammonium nitrate	80.0	NH ₄ NO ₃	2,479	198.3
Hexogen (cyclonite)	222.1	C ₃ H ₆ N ₆ O ₆	5,647/5,360	1,254.2/1,190.5
Trinitrobenzene	213.1	C ₆ H ₃ N ₃ O ₆	3,876	826.0
Nitroglycerin	227.1	C ₃ H ₅ N ₃ O ₉	6,671	1,515.0

$$\begin{aligned}\Delta u &= 1 \cdot 0 + 6 \cdot (-111,9) + 2,5 \cdot 0 + 1,5 \cdot 0 - 1 \cdot (-49,74) = -621,66 \frac{\text{kJ}}{\text{mol}} \\ &= -2738,6 \frac{\text{kJ}}{\text{kg}}\end{aligned}$$

The result is the heat of explosion, for which -2710 kJ kg^{-1} is found in [5]. Still to be added is the term describing the expansion work. Based on Eqs. (2.49) and (2.50) we have

$$\begin{aligned}ds &= 1 \cdot 0.00574 + 6 \cdot 0.197556 - 8.3145 \cdot 10^{-3} \cdot 6 \cdot \ln \frac{6}{10} + 2.5 \cdot 0.130571 - 8.3145 \cdot 10^{-3} \cdot 2.5 \cdot \ln \frac{2.5}{10} \\ &\quad + 1.5 \cdot 0.1915 - 8.3145 \cdot 10^{-3} \cdot 1.5 \cdot \ln \frac{1.5}{10} - 1 \cdot 0.27 = 1.6127 \frac{\text{kJ}}{\text{mol K}} = 7.103 \frac{\text{kJ}}{\text{kg K}}\end{aligned}$$

We obtain the explosion energy according to Eq. (2.46)

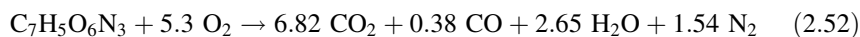
$$dw = df = du - Tds = -2738,6 - 298,15 \cdot 7,1013 = -4855,9 \frac{\text{kJ}}{\text{kg}}$$

In [5] the explosion energy is stated to be $-4,850 \text{ kJ kg}^{-1}$. The heat of combustion is determined in Example 2.15.

Details on selected other explosives are provided in Table 2.33

Example 2.15 Determination of the heat of combustion of TNT

Determine the heat of combustion of TNT. A look at Table 2.31 shows that TNT has a negative oxygen balance. Therefore the decomposition reaction is substoichiometric. Hence, the products may still react with oxygen and then release heat. If this is accounted for, the following equation of reaction can be established [45]



Solution

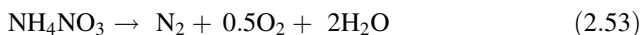
The difference of the internal energies is

$$\begin{aligned}\Delta u &= 6.8 \cdot (-393.8) + 0.38 \cdot (-111.9) + 2.65 \cdot (-240.8) + 1.54 \cdot 0 - 1 \cdot (-49.74) - 5.3 \cdot 0 \\ &= -3408.22 \frac{\text{kJ}}{\text{mol}} = -15014.19 \frac{\text{kJ}}{\text{kg}}\end{aligned}$$

In [5] $-1,5132 \text{ kJ/kg}$ is given as heat of combustion.

Example 2.16 Generation of gaseous reaction products

Determine the volume of gas produced by the explosion of 1 kg of ammonium nitrate (molar mass 80.04) (water is usually considered as being in gaseous state although the molar standard volume of $22.414 \text{ m}^3 \text{ kmol}^{-1}$ refers to 0°C and 101.325 kPa).

*Solution*

Calculation of the number of moles in 1 kg of ammonium nitrate:

$$N = \frac{1,000 \text{ g}}{80.04 \frac{\text{g}}{\text{mol}}} = 12.49$$

According to the reaction Eq. (2.53) 1 mol of ammonium nitrate reacts to form 3.5 mol of product. Hence we have

$$V = 12.49 \cdot 3.5 \text{ mol} \cdot 22.414 \cdot 10^{-3} \frac{\text{m}^3}{\text{mol}} = 0.979 \text{ m}^3$$

□

Example 2.17 Calculation of the peak overpressure of an explosion of TNT

We consider an explosion of TNT according to the reaction Eq. (2.51) at an initial temperature of $T_a = 298.15 \text{ K}$.



Determine the maximum pressure of its detonation.

Solution

The entire heat release calculated as the difference between the energies of formation of the products and the reactants must be equal to $c_v \Delta T$.

$$\Delta u_{\text{TNT}} = \int_{T_0}^{T_e} (1 \cdot c_C + 6 \cdot c_{v,\text{CO}} + 2,5 \cdot c_{v,\text{H}_2} + 1,5 \cdot c_{v,\text{N}_2}) dT$$

The specific heat capacity of graphite is taken as the constant value $c_C = 8.5 \text{ J/(mol K)}$. All the other heat capacities depend on temperature. In order to determine them recourse is had to the information of Sect. 2.1.1.8. Use is made of the facts that the integral of c_p over temperature is the enthalpy and that the relationship

$$c_v = c_p - R_m$$

holds between the heat capacities with $R_m = 8.3145 \text{ J/(mol K)}$ being the universal gas constant. Hence we have

$$\Delta u_x(T_e) = h_x^0(T_e) - h_{x,298,15}^0 - R_m \cdot (T_e - 298,15)$$

with x representing the respective material. Using Eq. (2.51) the temperature T_e is found iteratively from the transcendental equation

$$\Delta u_{\text{TNT}} = 1 \cdot c_C \cdot (T_e - T_0) + 6 \cdot \Delta u_{\text{CO}} + 2.5 \cdot \Delta u_{\text{H}_2} + 1.5 \cdot \Delta u_{\text{N}_2}$$

This is done using a root finding method (vid. [24]). With the above results and the help of Table 2.32 $T_e = 2,665.6 \text{ K}$ is obtained. Then we obtain according to Eq. (2.39)

$$p_s = \frac{1 \text{ bar} \cdot 10 \cdot 2665.6 \text{ K}}{1 \cdot 298.15 \text{ K}} = 89.4 \text{ bar}$$

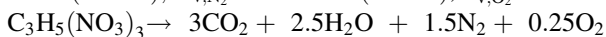
Using Eq. (2.40) and the data from Table 2.31 we have

$$p_s = 9.9792 \cdot 10^{-10} \cdot 1600 \cdot 6900^2 = 76.02 \text{ bar}$$

□

Example 2.18 Calculation of the maximum pressure of the explosion of nitroglycerin

Nitroglycerin explodes according to the reaction equation given below. The following mean heat capacities are to be used: $c_{v,\text{CO}_2} = 51.03 \text{ J/(mol K)}$, $c_{v,\text{H}_2\text{O}} = 43.12 \text{ J/(mol K)}$, $c_{v,\text{N}_2} = 27.34 \text{ J/(mol K)}$, $c_{v,\text{O}_2} = 30.08 \text{ J/(mol K)}$.



Solution

$$\begin{aligned} \Delta u_{\text{Nitroglycerin}} &= 3 \cdot (-393.8) + 2.5 \cdot (-240.8) + 1.5 \cdot 0 + 0.25 \cdot 0 - (-349.71) \\ &= -1433.68 \text{ kJ/mol} \end{aligned}$$

Using this value and following the procedure of Example 2.17 one obtains

$$T_e = 4633.5 \text{ K}$$

Equation (2.39) gives the maximum pressure

$$p_s = \frac{1 \text{ bar} \cdot 7.25 \cdot 4633.5 \text{ K}}{1 \cdot 298.15 \text{ K}} = 112.7 \text{ bar}$$

Using Eq. (2.40) and the data from Table 2.31 we obtain

$$p_s = 9.9792 \cdot 10^{-10} \cdot 1590 \cdot 7600^2 = 91.65 \text{ bar}$$

2.6 Toxic Materials

Toxic materials or poisons are substances which can harm health. Their impact depends on the type of material and exposure, which may range between short time exposures to high concentrations and long-term exposures to low concentrations during an entire working life. Toxic substances can enter the body through the following routes of exposure:

- inhalation;
- ingestion;
- external contact with skin resorption.

The following effects are then to be expected:

- irritations, allergies
 - respiratory tract,
 - skin,
 - eyes;
- narcosis;
- asphyxiation
 - simple,
 - chemical;
- systemic damage, harm to the bodily control functions;
- cell mutations;
- cancer;
- genetic damage.

2.6.1 Limiting Long-Term Exposure

The physician K.B. Lehmann observed in the course of his factory inspections and as a result of animal and other experiments in the years 1884 to 1886 that there exists an airborne concentration for any substance below which no occupational disease develops. This is true independently of the time of exposure. This realization led to the development of the MAK values (MAK: maximum occupational

Table 2.34 AGW values for selected materials of frequent use in the process industry [47]

Material	Workplace threshold value	
	ml m ⁻³ (ppm)	mg m ⁻³
Ammonia	20	14
Chlorine	0.5	1.5
Carbon monoxide	30	35
Carbon dioxide	5,000	9,100
Phosgene	0.1	0.41
Mercury	–	0.02
Sulphur dioxide	1	2.5
Vinyl acetate	5	18

exposure concentration; similar to OEL: occupational exposure limits in the U.K. and TLV: threshold limit values in the U.S.A.) [46].

These values nowadays are only of historical interest. Instead the Technical Rules for Hazardous Materials are used [47]. They contain threshold values for occupational exposure.² Table 2.34 gives the corresponding values for selected materials, which are frequently used in the process industry. The values apply to a working life with a five-day week and 8 h of daily work. They are called workplace threshold values (AGW). Additionally, there is a transgression factor catering for short-time exposure to higher concentrations (vid. [47]).

For practical applications it is often necessary to convert ppm into mg m⁻³ and vice versa. This is done by

$$C^* = \frac{1000 \cdot \frac{Z \cdot R_m \cdot T}{p}}{M} \cdot C \frac{\text{mg}}{\text{m}^3} \quad (2.54)$$

In Eq. (2.54) Z is the compressibility factor, R_m the universal gas constant in J/(mol K), T the temperature in K and M the molar mass of the respective material in g/mol.

Fixing thresholds below which no impact is to be expected encounters limitations in the case of carcinogenic substances. This is why recently a probability-related concept was proposed for such substances (vid. [49] and Sect. 8.2).

² The workplace threshold value (AGW) is the limiting value for a time-averaged concentration of a substance in the air at the workplace related to a given time period of reference. It indicates the concentrations for which acute or chronic harmful effects on health are not generally to be expected (Para. 3, Sect. 6 Hazardous Materials Ordinance [48]).

2.6.2 Limiting Short-Term Exposure

2.6.2.1 Threshold Values

During an accident large quantities of toxic materials may be released. Specific threshold values were developed for the resulting concentrations, since the threshold values for work life exposure are inappropriate. Among them figure AEGLs (Acute Exposure Guideline Levels) [50], ERPGs (Emergency Response Planning Guidelines) [51], TEELs (Temporary Emergency Exposure Levels) [52] and EEIs (Emergency Exposure Indices) [53]. These values are specifically devised for emergency planning.

The SEL (Seuil d'Effet Létal) [54] and DTL (Dangerous Toxic Load) [55] values are mainly targeted at land-use planning. Only the ACUTEX method of the European Community [56] provides values for land-use and emergency planning.

2.6.2.2 Probit Relations

Whilst threshold values merely enable one to take “good” or “bad” decisions a probit (“probability unit”)-relation allows one to assess the probability of a certain consequence, e.g. death, occurring due to a causative factor such as toxic exposure. For example, we have for the exposure to chlorine

$$Y = -17,1 + 1,69 \cdot \ln \left(\int_0^t C(t')^{2,75} \cdot dt' \right) \quad (2.55)$$

In Eq. (2.54) $C(t')$ denotes the variation with time of the chlorine concentration. Generally the time integral over a concentration is called dose. However, if an exponent $\neq 1$ is applied to the concentration we speak of load, e.g. in this case toxic load.

Probit relations are formulated such that they adopt the value $Y = 5$ for a damage probability of 0.5. This corresponds to the lethal dose 50, LD_{50} , a value at which 50 % of the affected individuals are expected to die.

The probability of damage then results from

$$P_{\text{damage}} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{Y-5} \exp\left(-\frac{x^2}{2}\right) dx = \phi(Y-5) \quad (2.56)$$

in Eq. (2.56) ϕ standard normal distribution (cf. [57]).

The advantage of using a probit relation is the higher degree of realism. The probability of damage usually grows with an increasing intensity of the damage-causing factor. The application of probit relations therefore is an appropriate way to make knowledge from areas like medicine and toxicology available and practicable for the engineer.

Appendix B gives probit relations for a number of materials used in the process industry. They are based on observations of accidents, experiments with animals and expert judgment. Hence, they are relations affected by uncertainties. However, no assessment of their magnitude is usually indicated.

Example 2.19 Calculation of probabilities of death and uncertainties

Calculate the probabilities of death for those substances, where several probit relations are given in Appendix B. The calculations are to be based on a concentration of 5,000 ppm and an exposure during 30 min. They reveal that uncertainties affect the probit relations.

Solution

The calculations are based on Eqs. (2.55) and (2.56). In conjunction with the equations of Appendix B the following results are obtained

<i>Ammonia</i>		
(B3a)	$Y = 6.4$	$P_{\text{death}} = 0.92$
(B3b)	$Y = 5.6850$	$P_{\text{death}} = 0.7533$
(B3c)	$Y = 1.9058$	$P_{\text{death}} = 9.9 \times 10^{-4}$
<i>Chlorine</i>		
(B7a)	$Y = 28.232$	$P_{\text{death}} = 1.0$
(B7b)	$Y = 44.575$	$P_{\text{death}} = 1.0$
(B7c)	$Y = 10.595$	$P_{\text{death}} = 1.0$
(B7d)	$Y = 8.3717$	$P_{\text{death}} = 0.9996$
<i>Hydrogen fluoride</i>		
(B11a)	$Y = 9.5099$	$P_{\text{death}} = 1.0$
(B11b)	$Y = 7.6551$	$P_{\text{death}} = 0.9960$
(B11c)	$Y = 4.1043$	$P_{\text{death}} = 0.1852$
(B11d)	$Y = 14.104$	$P_{\text{death}} = 1.0$
<i>Phosgene</i>		
(B17a)	$Y = 33.584$	$P_{\text{death}} = 1.0$
(B17b)	$Y = 24.661$	$P_{\text{death}} = 1.0$

□

Example 2.20 ERPG values and probabilities of death

Using the probit equations of Appendix B the probabilities of death are to be determined which correspond to the ERPG values³ of Table 2.35. An exposure time of one hour is to be used, which is the reference duration for the ERPG values.

³ ERPG-1: The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 h without experiencing more than mild, transient adverse health effects or without perceiving a clearly defined objectionable odour. ERPG-2: The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 h without experiencing or developing irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action. ERPG-3: The maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to 1 h without experiencing or developing life-threatening health effects.

Table 2.35 ERPG values [51] and corresponding probabilities of death

Substance	ERPG-1			ERPG-2			ERPG-3			Probability of death			Eq.
	ppm			ppm			ppm			ERPG-1	ERPG-2	ERPG-3	
Acrolein	0.05			0.15			1.5			0	0	5.6×10^{-9}	(B1)
Acrylonitrile	10			35			75			0	4.9×10^{-12}	2.1×10^{-4}	(B2)
Ammonia	25			150			750			0	0	5.7×10^{-7}	(B3a)
Benzene	50			150			1,000			0	0	0	(B4)
Bromine	0.1			0.5			5			0	0	1.3×10^{-13}	(B5)
Hydrogen cyanide	n.a.			10			25			–	0	1.1×10^{-16}	(B6)
Chlorine	1			3			20			0	0	0.1	(B7a)
Hydrogen chloride	3			20			150			0	8.7×10^{-15}	1.4×10^{-4}	(B8)
Ethylene oxide	n.a.			50			500			–	4.2×10^{-6}	1.6×10^{-2}	(B9)
Fluorine	0.5			5			20			0	1.3×10^{-8}	2.6×10^{-3}	(B10)
Hydrogen fluoride	2			20			50			0	0	0	(B11a)
Formaldehyde (>90 %)	1			10			40			0	1.5×10^{-9}	1.0×10^{-2}	(B12)
Carbon disulphide	1			50			500			0	0	1.1×10^{-16}	(B13)
Carbon monoxide	200			350			500			1.1×10^{-16}	3.7×10^{-10}	6.6×10^{-7}	(B14)
Methanol	200			1,000			5,000			1.6×10^{-7}	2.6×10^{-5}	1.4×10^{-3}	(B15)
Fuming sulphuric acid 65 %	2			10			120			0	0	6.4×10^{-3}	(B16)
Phosgene	n.a.			0.5			1.5			–	0	0	(B17a)
Phosphine	n.a.			0.5			5			–	5.9×10^{-5}	6.1×10^{-2}	(B18)
Hydrogen sulphide	0.1			30			100			0	1.1×10^{-8}	4.7×10^{-4}	(B19)
Sulphur dioxide	0.3			3			25			0	0	5.4×10^{-8}	(B20)
Toluene	50			300			1000			4.3×10^{-10}	8.3×10^{-6}	1.0×10^{-3}	(B21)

n.a: not appropriate

Solution

The solutions are based on Eqs. (2.55) and (2.56). In conjunction with the equations from Appendix B we obtain the results of Table 2.35. \square

Example 2.21 Toxic exposure in a building

If toxic gases are released in residential areas part of them penetrates into the buildings. Nevertheless a building may afford shelter, a circumstance which should be accounted for when assessing the possible number of persons killed or injured following a release. The extent to which a building provides protection depends on its air exchange rate, which in turn depends on the following factors:

- topographic situation,
- building quality,
- wind speed,
- wind direction,
- difference between temperatures indoors and outdoors.

According to [58] an air exchange rate of $k = 0.5$ to 0.8 per hour may be assumed if the windows are closed. The time variation of the concentration inside the building is regarded as proportional to the difference between the concentrations of the toxic substance inside the building, $c_i(t)$, and in its surroundings, $c_s(t)$. We then have

$$\frac{dc_i}{dt} = k \cdot (c_s - c_i) \quad (2.57)$$

If c_s is considered as constant and the initial condition $c_i(t = 0) = 0$, i.e. no toxic material inside the building at the beginning of the release, Eq. (2.57) has the following solution

$$c_i(t) = c_s \cdot [1 - \exp(-k \cdot t)] \quad (2.58)$$

However, with a real accident the concentration in the surroundings varies with time. This can approximately be described for releases close to the ground of gases which are lighter than air by (vid. Sect. 10.5)

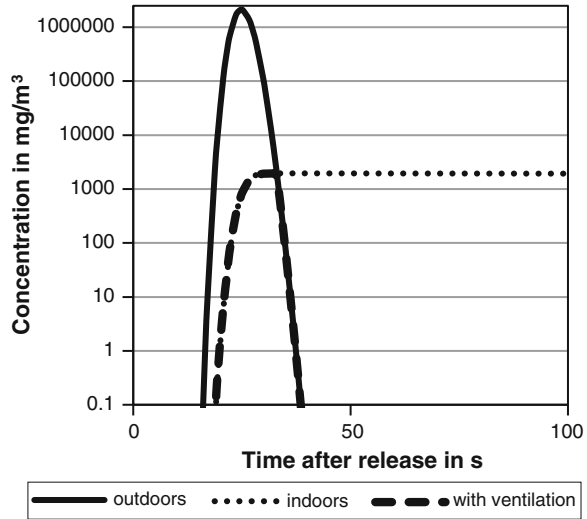
$$c_s(t, x_1, y_1, z_1) = \frac{2 \cdot Q}{(4\pi Kt)^{3/2}} \cdot \exp\left(-\frac{(x_1 - ut)^2 + y_1^2 + z_1^2}{4Kt}\right) \quad (2.59)$$

Table 2.36 Probabilities of death after a puff release of CO for different building qualities and mitigation strategies

Wind speed	$u = 2 \text{ ms}^{-1}; K = 0.5833 \text{ m}^2 \text{ s}^{-1}$				$u = 4 \text{ ms}^{-1}; K = 1.167 \text{ m}^2 \text{ s}^{-1}$		$u = 10 \text{ ms}^{-1}; K = 2.917 \text{ m}^2 \text{ s}^{-1}$	
Air exchange rate	Windows permanently closed	Windows opened when outside concentration lower than inside	Windows permanently closed	Windows opened when outside concentration lower than inside	Windows permanently closed	Windows opened when outside concentration lower than inside	Windows permanently closed	Windows opened when outside concentration lower than inside
0.7 h^{-1}	0.9998	0	0.8449	0	0.0007	0	0	0
3 h^{-1a}	0.9998	0	0.8438	0	0.0090	0	0	0

^aThis simulates a building of bad quality

Fig. 2.11 Time variation of the concentration after a toxic release outdoors and indoors without and with ventilation after the outdoor concentration drops below the indoor concentration ($u = 4 \text{ ms}^{-1}$)



The quantities in Eq. (2.59) have the following meaning:

- Q : released mass of toxic gas in kg
- x_1 , y_1 , and z_1 : coordinates of the building in m, assuming that the point of release is the origin of the coordinate system
- K is a parameter characterizing the atmospheric and topological conditions in the surroundings of the point of release, the eddy coefficient in m^2s^{-1}
- u the wind speed in m/s in the direction of x-axis, which is oriented in such a way that it connects the point release with the location of the building

Whilst it makes sense to seek shelter in a building and to close its windows immediately after the release it is preferable in the long term to open the windows and leave the building, when the outside concentration drops below the concentration inside the building.

The inhomogeneous linear differential Eq. (2.59) is solved numerically using the Runge-Kutta method of second order with variable time steps (cf. [25]).

Scenario for the calculation

Owing to tank failure there is a puff (instantaneous) release of 10,000 kg of CO. A building stands at a distance of 100 m in the direction of the wind. Determine the time-dependent concentrations and probabilities of death.

Solution

Equation (2.57) in conjunction with Eq. (2.59) is applied. The probability of death is calculated using the probit from Eq. (B14). The following input data is used:

$Q = 10,000 \text{ kg}$; $x_1 = 100 \text{ m}$; $y_1 = 0 \text{ m}$; $z_1 = 6 \text{ m}$

The results are shown in Table 2.36 and in Fig. 2.11. □

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