Ulrich Hauptmanns

Process and Plant Safety

2nd Edition

Springer Vieweg

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To Uta and Anton

Preface to Second Edition

The second edition of the present book provided the opportunity to thoroughly revise the text and to make a number of corrections. New examples resulting from inquiries of practitioners were added. The chapter on “appropriate safety distances” was extended by including experiences from the author’s consulting activities.

I would like to thank Prof. Dr. U. Stephan, Dr.-Ing. Arizal and Dipl-Ing. D. Möckel for their expert advice.

Schönebeck (Elbe), February 2020 Ulrich Hauptmanns

Preface to the German Edition

Quidquid agis prudenter agas, respice finem

Safety is a basic human need. That is why a modern society must ensure that industrial production is safe. The task of engineers dedicated to process and plant safety is to achieve this. They ensure that plants are designed for safety and built and operated safely and that people have safe workplaces. Only if this is fulfilled is the operation of industrial plants ethically acceptable.

Safety means that hazards are kept small. However, there is no possibility to eliminate them completely; for whatever is possible will occur with a certain probability.

In order to make engineered systems safe, the probability of hazards must be reduced as far as possible. This requires a structured approach that is based on experience as well as experimental and theoretical findings. In this book, the approach for analyzing and designing safe process plants is described. Starting points are possible hazards from material properties and operating conditions. The focus is placed on the qualitative and quantitative modelling of technical systems and the simulation of physical and chemical processes during operation and accidents. The material presented is extended and complemented by a number of examples and case studies, which refer to real plants or events.

A characteristic of analyses of process and plant safety is that the interdependencies within the engineered system, the influence of its components on one another and human interventions must be accounted for. A further characteristic is the stochastic nature of the processes to be analyzed, which renders it, for example, impossible to predict the moment of occurrence of an accident. These aspects are duly addressed.

Process and plant safety is interdisciplinary. Just as for building and operating a plant process, mechanical, electrical, and civil engineering as well as informatics have to be combined, plant safety needs these disciplines, too. This makes the selection of topics difficult and shows that experts for safety, who cannot possibly have a command of all these areas of knowledge, should address safety tasks in cooperation with specialists of the areas mentioned.

The selection of topics follows that of the model curriculum “Process and Plant Safety” of ProcessNet. My gratitude goes to my colleagues, Profs. A. Schönbucher,

H. W. Brenig, H. U. Moritz, and J. Schmidt as well as to Dr. O. Klais for instructive and vivid discussions when elaborating the curriculum and deciding on unavoidable omissions.

Safety needs foresight. It should not derive from trial and error as it did in the earliest days of engineering. An important tool is the elaboration of scenarios, i.e. potential developments of the future. This requires thought experiments to be performed, which must be based on a broad background of knowledge in engineering and natural sciences as well as of experimental results and the simulations of accidents.

The book provides students and practitioners with the necessary tools for analyzing processes and plants and designing them for safety. It makes use of knowledge in mathematics, physics, chemistry, as well as of thermal and fluid dynamics, as taught during the first semesters of engineering courses.

The text is based on courses that I have been offering for more than a decade and a half at the Otto-von-Guericke-Universität Magdeburg. Discussions with collaborators and students have contributed to it. I thank them for their dedication.

I gratefully acknowledge the expert advice of Professors U. Stephan and Y. Ding, and Drs. J. F. Bremen, V. Schröder, D. Jablonski, and Arizal, as well as that of Dipl.-Ing. P. Guterl and Dipl.-Stat. J. Peschke. To Dr. Arizal I am also obliged for the implementation of a large part of the figures. My profound gratitude is expressed to all the experts from industry who granted me access to their plants and shared their knowledge of industrial practice with me.

My thanks go to the Springer Verlag for the good cooperation and fine presentation of the book.

The author hopes that the book enables students and practitioners to acquire knowledge of modern methods of safety analysis and to contribute to the safety of processes and plants by using them. In doing so they should follow the advice from classical antiquity that I have placed in front "Whatever you do, do it with intelligence and with the outcome in mind."

Schönebeck (Elbe), Spring 2013 Ulrich Hauptmanns

Preface to the English Edition

The preparation of the translation gave me the opportunity to correct a number of minor mistakes and to occasionally formulate concepts in a somewhat clearer language. Wherever possible, German references were replaced by English ones. All of this should be of benefit to the reader.

Schönebeck (Elbe), Spring 2014 Ulrich Hauptmanns

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Introduction

1

Whoever demands absolute safety, ignores the law of life.

1.1 Introduction

The production of the process industry[1] often involves hazards. Their nature can be both physical and chemical. Physical hazards derive from operating conditions that may be extreme, such as very low or very high temperatures and pressures. Chemical hazards are those associated with the materials present in the process, which can be toxic, flammable, explosible, or release energy due to spontaneous[2] reactions. Indeed, it is the necessity to put the substances into a reactive state in order to enable one to produce the desired products that may lead to hazards.

A further complication stems from the fact that some of the properties of the substances can vary with changes of process parameters such as temperatures, pressures or concentrations, or that these changes may give rise to or favour unwanted side reactions, as was the case in the Seveso accident, where larger quantities of dioxin than usual were generated and released to the environment (cf. [1]).

In addition, dangerous properties, if not present under nominal operating conditions, may evolve upon contact of process media with auxiliary media such as coolants or lubricants. After release, reactions with substances present in the environment, e.g. the humidity of the air, may give rise to dangerous properties.

Nevertheless a concretization of the hazard potential is normally not to be expected, since the design, construction, erection, and operation of the plants are

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[1] The term “process industry” comprises firms from the chemical, petrochemical, pharmaceutical and food industries as well as the production of steel, cement and the like.

[2] “Without apparent reason” from the Latin word sponte “from its own accord”.

U. Hauptmanns, *Process and Plant Safety*,
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based on the state of technology, respectively safety technology[3] (cf. [2]). Hence, they are supported by a broad base of experience, which, depending on the country, is reflected by the respective laws, rules, and regulations. A good overview of this topic is provided by the Guideline Plant Safety [3].

According to [3] the design of a plant has to be such that the containment of hazardous substances inside the plant, i.e. vessels, pipework, reactors etc. is ensured. This does not only result in demands on the mechanical resistance of the components of the plant, but requires safety systems to be introduced, which in case of undesired loads (mostly excessive temperatures and/or pressures) are to guarantee the integrity of the containment by pressure relief, emergency trips, emergency cooling etc.

If all components were to function with perfection and, in addition, the measures of safety management were perfect plants would be absolutely safe.

This is, however, not the case and cannot be achieved. Apart from the—although remote—possibility of wrong dimensioning (e.g. walls too weak) components of engineered systems can fail, humans can commit errors in operating the engineered system or external threats such as flood, storm or lightening may lead to failures within the plant. Thus, temperature and pressure increases or other damaging events may be triggered. In addition, it is conceivable that safety systems are not available due to component failures. Probabilities for such events may be assessed. However, the instant in time of a component failure, human error or destructive external event cannot be predicted.

Hence, despite careful design, construction and operation of plants accidents cannot totally be avoided. Whatever may happen will happen with a certain probability. Therefore the probability of an accident[4] can only be reduced by appropriate measures. To achieve this is the objective of risk management.

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[3] State of safety technology: the state of development of advanced processes, installations and procedures that permit one to take for granted the practical aptitude of a measure for avoiding accidents or limiting their consequences. When determining the state of safety technology comparable processes, installations and procedures have to be considered that have been successfully applied in practice [4] (translated by the author).

[4] Accident: an event such as an emission, a fire or an explosion of major impact that leads to a disturbance of the specified operation* in a site or a plant subject to this ordinance (Author's remark: this refers to the Major Accident Ordinance [4]) that leads immediately or at a later stage to a serious hazard or material damage within or outside the site involving one or several hazardous substances as listed in annex VI part 1 para I no. 4.

*Specified operation is the operation for which a plant is designed and appropriate. Operating regimes not covered by the valid license, posterior impositions or applicable legal requirements do not belong to the specified operation. The specified operation comprises the

- normal operation including necessary human interventions such as the taking of samples and including the storage with filling, transfer and refilling procedures,
- plant commissioning and its start-up and shut-down,
- trial operation,
- maintenance, inspection, repair and cleaning work as well as
- periods of temporary stand-still [8] (translated by the author).

Yet, a risk remains, i.e. a probability (or more precisely an expected frequency) that a damage of a certain type and impact occurs. In a process plant this may be a fire, an explosion or a toxic release, which may affect both humans and the environment. It is the price to be paid for the desired product. The damage can affect employees, the population at large or both, as becomes evident from Table 1.1.

The protection of the employees is ensured by a number of laws, regulations and guidelines (cf. [5, 6]). The justified interest of the population in safety, the protection according to the Federal Pollution Control Act (BImSchG) [7], is guaranteed by the licensing procedure.

Two fundamental approaches in licensing are conceivable:

(1) the license is granted solely on the basis of fulfilling the above mentioned requirements; risk is not assessed.
(2) In addition to (1) statements on risk have to be made and certain risk criteria to be met.

The procedure according to (1) is used in the Federal Republic of Germany and that of (2), for example, in the Netherlands.

It has to be emphasized that the operating systems of a plant are dimensioned by the same procedure with both approaches. Requirements for the systems are specified, for example, the quantity of heat to be extracted from a reactor for an exothermic reaction. The corresponding calculations are performed using mathematical models reflecting the underlying laws of nature. Results in this case may be, for example, the power of the coolant pump, the necessary surface for heat transfer, or the pipe diameters. This procedure is called deterministic.

The safety design of a plant results from extensive analyses (cf. [2]) to be discussed later. The dimensioning of safety systems is also carried out deterministically. It is based on the concept of disturbances that have to be avoided,[5] for example a cooling failure in a reactor for an exothermic reaction. This is the basis for determining the type and capacity of the safety system coping with it. Its quality and degree of redundancy may then be determined

(1) by indeterminate legal terms in regulations (cf. [4]) such as “reliable measuring device” or
(2) probabilistically[6] based on risk criteria.

As mentioned before, the approach according to (1) is that used so far in Germany. However, in the meantime probabilistic requirements for safety systems are derived from risk considerations in fulfilment of the standards on functional safety [10–12]. This corresponds to (2).

---

[5] In the field of nuclear engineering this is referred to as “design-basis accident”.

[6] Based on probability considerations derived from the Latin word probabilis: assumable, likely, credible.

Table 1.1 Some accidents in the process industry [9]

Date	Place	Event	Consequences		Comment
			Workforce	Population	
June 1st, 1974	Flixborough, U.K.	Explosion of a cloud of cyclohexane	28 killed, 36 gravely injured	53 gravely injured	All buildings in a radius of 600 m destroyed, presumably an unprofessional repair
July 10th, 1976	Seveso, Italy	Release of 2,3,7,8- Tetrachlorodibenzo-dioxin		220,000 persons exposed, 736 inhabitants evacuated, >250 cases of chloracne	2000 ha contaminated, 81,000 animals died or were forcedly slaughtered
December 2nd, 1984	Bhopal, India	Release of 23–42 t of methyl isocyanate; water used for cleaning initiated an exothermic reaction with temperature and pressure rise		16,000 persons killed, 170,000–600,000 poisoned	>4000 animals died
October 23rd, 1989	Pasadena, U.S.A	Explosion of a cloud of isobutene, ethylene, hexane, hydrogen released during maintenance of a polyethylene reactor	23 killed, 314 injured	Housing damage within a radius of 8 km	Earthquake intensity equivalent to 2,4 t TNT, magnitude 3,5 Richter
May 13th, 2000	Enschede, Netherlands	Explosion in a fireworks depot	20 killed, among them 4 firemen	400 houses destroyed, 1250 people homeless	Spreading of an initial fire of unclarified cause
September 21st, 2001	Toulouse, France	Explosion of 20–100 t of rejects of ammonia nitrate	22 killed	8 killed, 2450 injured, 26,000 houses damaged	Earthquake intensity equivalent to 20–40 t TNT, magnitude 3,4 Richter, perceived up to a distance of 75 km
June 20th, 2002	Kingsville, Canada	Fire in a plastics factory		2000 evacuated for three days, time after which the fire was extinguished	Recommendation not to allow children to play outdoors and not to consume garden vegetables

(Fortsetzung)

Table 1.1 (Fortsetzung)

Date	Place	Event	Consequences		Comment
			Workforce	Population	
November 28th, 2002	Mestre, Italy	Overpressure failure of a vessel containing a mixture of toluene and 2,6 diisocyanate producing a fire	4 translated by pressure wave, slightly affected	Cloud of fumes with negligible effect, bituminous emission from an outlet contaminating 8 km of beaches	A similar vessel suffers a consequential explosion (Domino effect)
January 6th, 2005	Troisdorf, Germany	Pentrite explosion during maintenance work in an explosives factory	1 killed		
March 23rd, 2005	Texas City, U.S.A.	Vapour cloud explosion in a refinery	15 killed, 170 injured	Deflagration noticed up to a distance of 8 km	Hydrocarbon release from a blowdown drum, ignition by a starting truck
December 11th, 2005	Buncefield, U.K.	Explosion (unexpectedly high overpressure) and fire in an oil storage terminal		43 injured	Overfilling of a tank from a pipeline with a subsequent release of 300 t of petrol
March 17th, 2008	Cologne, Germany	Escape of ethylene followed by fire when maintaining a pipeline inside a process plant	None	None	Fire affects nearby acrylonitrile storage, 300 t of ethylene and 1200 t of acrylonitrile were burnt; 1180 fire fighters involved
October 23rd, 2009	Bayamon, Puerto Rico	Fire and explosion in a fuel storage	Several persons injured including 3 rescue workers	Evacuation of 1500 persons from their homes	Petrol cloud of 600 m diameter formed before ignition, explosion causing an earthquake of 2.8 on the Richter scale, buildings damaged in a radius >1.6 km
November 4th, 2010	Paderno Dugagno, Italy	Explosion and violent fire in a storage of paints and spent solvents	3 killed, 4 injured	Population urged to stay indoors	Serious flaws in the safety systems
April 20th, 2011	Pardubice, Tcheque Republic	Explosion of nitroglycerine in a factory for explosives	4 presumably killed, 9 injured	Glass breakage within a radius of 4 km	Probably human error in mixing nitroglycerine and nitrocellulose

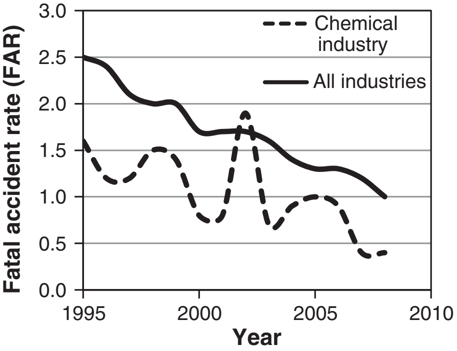

Fig. 1.1 Fatal accident rate *FAR* (fatalities per 10^8 working hours) for the chemical industry and the industry in general in Germany [16]

There is a recent tendency to measure the safety achievements by indicators (so-called key performance indicators) (cf. [13, 14]). These refer on the one hand to past performance (“lagging indicators”) and on the other to future performance (“leading indicators”).

In order to give an impression of standards achieved in the German process industry the following assessment is made. The accident statistics [15] shows that there was no fatal accident involving members of the public during 10 years of operation of the 7800 plants subject to the Major Accident Ordinance [14]. On this basis a Bayesian zero-event statistics leads to a coarse assessment of $6.4 \times 10^{-6}\ a^{-1}$ for a fatality outside a plant (vid. Example 9.4).

Figure 1.1 provides an impression of the safety performance concerning labour accidents comparing the chemical industry with figures for the industry at large.

Plant and process safety encompasses all the areas required for designing and building a process plant and implementing the corresponding processes (amongst them process, mechanical, and civil engineering). As a rule time-dependent processes have to be treated, since we are usually concerned with deviations from nominal operating conditions. The latter are considered as safe if a rigorous implementation of safety has accompanied the design and erection of a plant and is a permanent concern during its operation. The compliance with these assumptions should, of course, be checked in the context of a safety analysis.

Safety deals with stochastic events, for example the moment of occurrence of an accident, and stochastic boundary conditions (e.g. the weather at that moment). These together with lacks of knowledge about some of the phenomena to be described and imperfections in models and input data lead to uncertainties, which are normally compensated by safety factors and often lead to procedures based on conventions.

The treatment of uncertainties has substantially progressed in recent years (cf. [17–27]). However, their detailed theoretical treatment is beyond the scope of the present text, so that only procedures with particular relevance for practical applications are explained.

In what follows the physical and chemical phenomena causing the hazard potential of process plants are treated in Chaps. 2 and 3. Chapters 4, 5, 6 und 7 are dedicated to engineered and organizational measures that are devised to avoid that the hazard potential harms employees and the public at large. Chapters 8, 9 und 10 deal with the determination of engineering risks. In this context the methods of plant system analysis and models for assessing accident consequences are presented. They serve to identify hazard potentials and to develop concepts for coping with them. Hence, they influence the safety design of plants and their safe operation. An important aspect of the safe design of plants is the concept of "functional safety", which is treated in Chap. 11. Finally, Chap. 12 is devoted to the determination of appropriate safety distances between industrial installations and the surrounding population, which may be an additional safeguard for reducing the consequences of an accident.

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Hazardous Properties of Materials

2

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 that 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 that 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.

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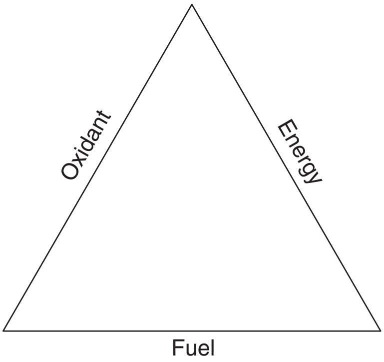

Fig. 2.1 Fire triangle

Example 2.1 Empirical frequencies for fires and explosions

The ARIA-databbase 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 to be 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 theses limits are referred to as the lower and upper limits of flammability (LFL and UFL) (vid. [4]). They represent the volume ratio[1] 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])

$$\mathrm{LEL} = 0.55 \cdot \mathrm{c_{st}} \tag{2.1}$$

$$\mathrm{UEL} = 3.50 \cdot \mathrm{c_{st}} \tag{2.2}$$

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

$$\mathrm{C_mH_xO_y + z \cdot O_2 \rightarrow m \cdot CO_2 + \frac{x}{2} \cdot H_2O} \tag{2.3}$$

we have

$$\mathrm{z = m + \frac{x}{4} - \frac{y}{2}} \tag{2.4}$$

and hence

$$\mathrm{c_{st} = \frac{100}{1 + z/0.21}} \tag{2.5}$$

---

[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

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])

$$\mathrm{UEL_p} = \mathrm{UEL_{0.1\,MPa}} + 20.6 \cdot (\log \mathrm{p} + 1) \tag{2.6}$$

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 $\mathrm{UEL_{0.1\,MPa}}$.

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

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**

[a] since 100% is the maximum, the value is merely a formal result
[b] measured at an initial pressure of 50 bar

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

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

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.

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)
[a] Temperatures up to 400 °C
[b] Temperatures up to 250 °C

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

$$\mathrm{LEL} = \frac{1}{\sum_{i=1}^{I} \frac{y_i}{\mathrm{LEL}_i}} \tag{2.8}$$

$$\mathrm{UEL} = \frac{1}{\sum_{i=1}^{I} \frac{y_i}{\mathrm{UEL}_i}} \tag{2.9}$$

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 (independence does often not apply since values from the same source are quoted in several references). Then the explosion limit may be assumed to be a random variable, i.e. a variable that adopts certain values with certain probabilities. 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.

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

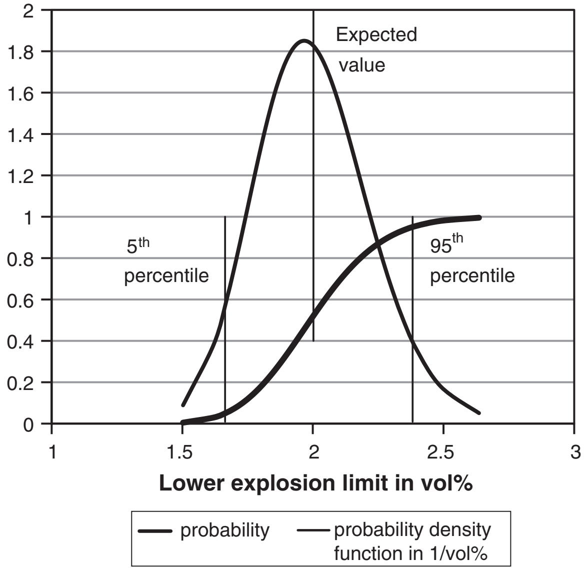

Fig. 2.2 Probability and probability density of the lower explosion limit of propane

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) to (2.5). The results are compiled in Table 2.4.

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 2.4 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_2H_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