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Inerting in the chemical
industry.

Imprint.

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Preface.

Industrial gases play an important role in the chemical industry. Key applications include reaction and maintenance processes, safety measures and environmental protection.

Chemical process, plant and apparatus inerting is often critical to personal, material and plant safety. Hence inerting is extremely common in both the chemical industry in particular and the gases industry in general.

Many application engineers in the gases industry, as well as technicians, engineers and chemists working in the chemical industry, would welcome a reference guide outlining various inerting methods, their range of applications and the associated hazards. The aim of this handbook is to help meet the need for information in this area.

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1. Introduction.

There are many chemical processes where it is necessary to:

- prevent explosions
- eliminate undesired reactions
- keep moisture away from products and
- ensure safety during maintenance work.

These goals cannot always be achieved through technology and equipment design alone and so engineers often also rely on inert gases and special inerting equipment. Inerting is done to minimise the level of oxygen in a given space and prevent oxygen and/or moisture from coming into contact with reactive or adsorptive products. Nitrogen is the gas most commonly used for inerting.

Less frequently, carbon dioxide or other gases may also be used. The basic principle entails fully or partially replacing air, which contains oxygen and often moisture as well, or a flammable and/or poisonous gas with an inert gas.

There are many situations in which inerting is the only way to meet safety standards during industry processes and maintenance. In other cases, inerting is used to maintain and improve product quality. Fields that make use of inerting include refining, basic chemistry, petrochemistry and the manufacture of speciality and fine chemicals.

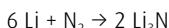
2. Gases used for inerting.

Nitrogen and carbon dioxide are the most widely used gases for inerting. Other gases such as argon and helium are applied in certain instances and some industrial applications use steam and exhaust gases.

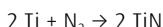
Criteria that influence the choice of inert gas include:

- Risk of fire and explosion and/or their impact or behaviour
- Effects on product and exhaust gas
- Cost
- Availability
- Security of supply

Although nitrogen and carbon dioxide are not fully inert, they are the gases of choice. At room temperature, nitrogen reacts with a very small number of substances, for example with lithium to form lithium nitride.



At temperatures ranging between 400 °C and 1800 °C, nitrogen can react with magnesium, silicon, titanium and other metals to form nitrides:



Reactions with oxygen occur only at very high temperatures.

By comparison, carbon dioxide reacts with a longer list of substances, including strong bases, amines, anhydrous ammonia, lithium, potassium, sodium, magnesium, beryllium, aluminium, chromium, manganese, titanium, uranium and acrolein. Since the decomposition temperature of carbon dioxide is 2000 °C, this is rarely an issue. A rise in pressure will, however, increase the solubility of this gas.

Noble gases are usually too expensive to be used for inerting and do not perform as effectively as nitrogen. They are, however, frequently used for inerting light metal dust. Argon, for example, is used to prevent aluminium dust explosions and in the extinguishing systems for such explosions (VDI Reports No. 2024, 2008).

If steam is used for inerting, the condensation that sometimes forms can compromise the inertization.

In the shipping industry, readily available exhaust gas is used in oil tanks, requiring careful control of the fuel to air ratio.

The specific heat of a given inert gas determines its effectiveness. The higher the specific heat, the better the inerting performance. Table 1 shows the respective values [1].

Table 1: Specific heat of selected inerting agents according to [1] at 0 °C and at constant pressure

Inerting agent	Specific heat* (Btu/(lb mole/°F))	Specific heat* (kJ/kmol/K)
Nitrogen	7.0	29.308
Carbon dioxide	8.8	36.844
Helium	5.0	20.934
Argon	5.0	20.934
Steam	17	71.176

* Values at constant pressure; steam at 27 °C, other values at 0 °C

The molecular structure of inert gases has a direct impact on their effectiveness. Carbon dioxide is a triatomic molecule, nitrogen is a diatomic molecule and argon and helium are monatomic molecules. Polyatomic molecules can absorb more energy because they contain a larger number of free molecular degrees of oscillation [2].

The inerting effect thus decreases in the following order:

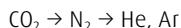


Figure 1 shows the level of effectiveness of inerting agents, taking the flammability of methane as an example.

The reason for this is that dilution with an inert gas that has a higher specific heat capacity reduces the area susceptible to flammability. By this logic, carbon dioxide again would be favoured over nitrogen, because a smaller volume of inert gas would be needed. In most cases, however, nitrogen is favoured for the following reasons [2]:

- Carbon dioxide is capable of reacting with a much larger number of substances than the other inerting gases.
- Carbon dioxide is soluble in aqueous products.
- It is corrosive in the presence of moisture.
- If the pressure drops sharply, carbon dioxide “snow” can form.
- Environmental regulations may apply when CO₂ is emitted into the atmosphere.

Table 2: Density of selected gases [2] and their densities relative to air

Type of gas	Density in kg/m ³ at 1013 mbar and 0 °C	Density relative to air
Air	1.293	1.0
Nitrogen	1.2505	0.967
Hydrogen	0.0899	0.0695
Argon	1.7837	1.38
Oxygen	1.429	1.105
Carbon dioxide	1.9767	1.529

Density also plays a particularly important role. If the density of the inert gas is greater than the density of the gas to be displaced, it is possible that the headspace above the injection point of the inert gas will not be inerted. This problem can be solved either by thoroughly mixing the inert gas inside the vessel or choosing an inert gas with a different density.

Table 2 shows the density of selected gases and how they compare with the density of air.

Table 3 presents some of the main properties of nitrogen and carbon dioxide of relevance to inerting.

The attached gas selector contains further information on nitrogen, carbon dioxide and argon. Since carbon dioxide has special properties, attention should be paid to its phase diagram (figure 2).

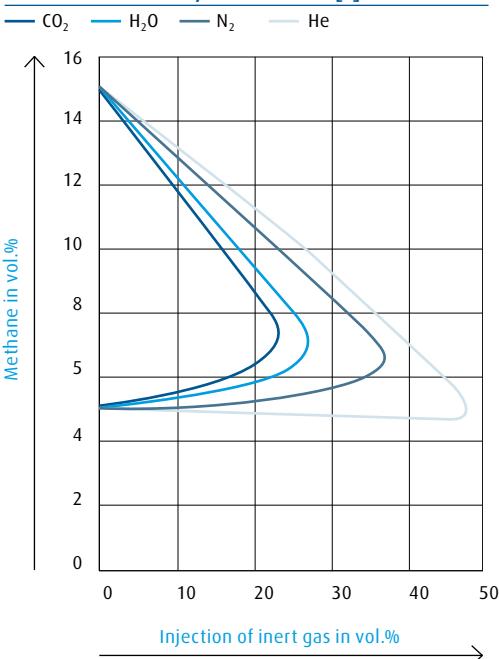
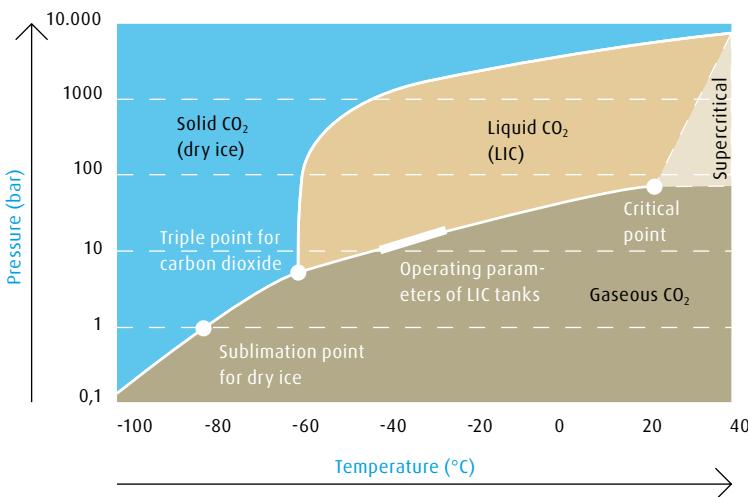
Figure 1: Influence of various inerting agents on the flammability of methane [1]

Table 3: Main properties of nitrogen and carbon dioxide [4]

Properties	Nitrogen	Carbon dioxide
Detectability by senses	Colourless and odourless	Colourless and odourless
Reactivity	Inert because of N≡N	Inert because of O=C=O
Flammability	Non-combustible	Non-combustible, fire-extinguishing
Molar mass	28 g/mol	44 g/mol
Threshold limit value *		5000 ppm
Density at 1 bar, 0 °C	1.250 kg/m ³	1.977 kg/m ³
Boiling point at 1 bar	-195.8 °C	
Melting point at 1 bar	-209.9 °C	-56.6 °C (triple point)
Sublimation point at 1 bar	Not applicable	-78.5 °C
Critical point	-147.2 °C (33.94 bar, 314 kg/m ³)	31.2 °C (73.83 bar, 466 kg/m ³)
Solubility in liquids at 1 bar, 15 °C	Solubility in water: 20 mg/l	Solubility in water: 2,000 mg/l
Health impact	Cold gases/vapours are denser than air, risk of suffocation	Harmful at higher concentrations, lethal when > 8% by vol.

*max conc. value at workplace occupational exposure limit (OEL)

Figure 2: Phase diagram of carbon dioxide

3. Overview of inert gas production methods.

Nitrogen and argon are obtained from air. Figure 3 shows the gas composition of dry air.

Nitrogen

Air is separated using membrane technology, pressure swing adsorption and cryogenic rectification. These methods differ not only in terms of the underlying separation technology, but also in terms of target applications and costs. For details, see table 4.

Membrane and pressure swing adsorption plants are suitable for small to mid-volume nitrogen users where demand fluctuates widely. If high purity nitrogen is required in large quantities, the cryogenic rectification method is the only valid option.

The oxygen content in the air greatly influences the energy input needed to separate the nitrogen in the membrane separation and pressure swing adsorption techniques. Figures 4, 5 and 6 show typical plants for cryogenic air separation, pressure swing adsorption and membrane separation.

Figure 3: Composition of dry air [5]

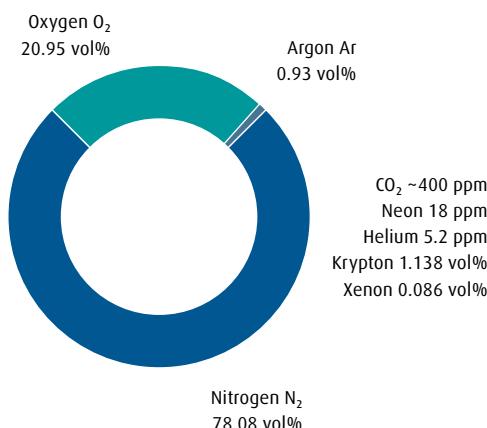




Figure 4: Cryogenic air separation plant



Figure 5: Adsorption plant

Table 4: Overview of technologies used to generate nitrogen [5]

Capacity in Nm ³ /h	Purity	Separation technology	Operating range
1-1000	< 99.5%	Membrane	30-100%
5-5000	< 99.99%	Pressure swing adsorption	30-100%
200 to 400,000	Down to ppb purity levels	Cryogenic rectification	60-100%



Figure 6: Small membrane separation plant

Noble gases

Helium, neon, argon, krypton, xenon, radioactive radon and synthetic ununoctium all belong to the group of noble gases. These are monatomic gases with low reactivity and are found in air. Helium is also sourced from natural gas in significant volumes.

Since argon is the most widely used noble gas for inerting, more attention will be given to its production process. Pure argon is sourced exclusively from air. Argon gas is not separated from the main constituents of air in the main air separation fractionating column, but in a separate argon column. Here, a rectification process initially produces crude argon, which still contains around 3–5% oxygen and 1% nitrogen. The crude argon is then purified in a number of stages. The gas mixture is first warmed to room temperature and compressed to a pressure of 4–6 bar. Hydrogen is then injected to remove the residual oxygen.

The hydrogen reacts with the oxygen in the presence of the noble metal catalysts to form water. In a further column, the argon, which has become concentrated at the bottom of the column, is separated from the remaining nitrogen so that the resulting gas has a purity of 99.9999% [5].

Argon can also be captured during ammonia and synthesis gas production processes, for example during methanol production. In these processes, which rely on air as the feedstock, argon and other noble gases are enriched and can be isolated from the gas mixture. Here too, the various gases are separated by adsorption or rectification, leaving pure argon.

Carbon dioxide

Carbon dioxide is obtained from natural sources and purified, or procured by gas companies from the chemical industry. Carbon dioxide is usually separated from combustion gases. Generator gas, for instance, contains 16–18% carbon dioxide. Processing of this crude gas can be done in the following stages:

1. Water-irrigated scrubbing to remove dust and sulphur dioxide
2. Dissolution of carbon dioxide in a solvent, such as methanol
3. A heating step to release the carbon dioxide from the loaded solvent
4. Compression step to liquefy the released carbon dioxide for transport in railcars or tankers.

Figure 7: Gas cylinders



Supply modes

Nitrogen is supplied in several different modes:

- Nitrogen in cylinders/cylinder bundles (10 l, 200 bar; 50 l 300 bar) (figure 7), purity grades: 4.6, 5.0, 5.3, 5.6, 6.0 and 7.0
- Liquid nitrogen (LIN) in tank systems, typical purity: 99.999% by vol., nitrogen capacity: 3,000 to 80,000 l
- Gaseous nitrogen (GAN) via pipelines or on-site plants
- Nitrogen mixed with other gases, for example synthetic air (20% O₂ and 80% N₂)

For larger inerting one-off jobs that require large amounts of nitrogen, e.g. during revamps, high-capacity mobile systems can deliver a stable supply of this gas.

The following parameters are possible:

- Pressures up to 700 bar
- Volume flow rates up to 25,000 Nm³/h
- Temperatures up to 400 °C

Figure 8 shows a mobile tank system.

Carbon dioxide is also supplied in pressurised gas cylinders or tankers. The pressure in the cylinder is temperature-dependent. The value is 52 bar at a temperature of 15 °C. The gas is transported in tankers at a temperature between -20 and -30 °C. The pressure would then be in the range from 20 to 14 bar.

Given the wide range of production and supply options available, an optimum solution can be found for each customer's individual needs.

Figure 8: Mobile high duty vaporiser



4. Applications of industrial inerting gases.

The chemical industry uses a wide range of substances, technologies and apparatus. Consequently, the spectrum of inerting applications using nitrogen, carbon dioxide and argon is equally broad. Inerting is used in particular for:

- Reactors, stirring tanks
- Centrifuges and vacuum filters
- Grinding and mixing plants
- Tank farms, vessels
- Dryers, silos
- Filling facilities
- Oil and fuel pipelines
- Industrial services

The main aims of these inerting activities are to:

1. Prevent explosive atmospheres from forming in apparatus such as reactors
2. Ensure safe startup and shutdown of plants and apparatus
3. Avoid explosion risks during storage and transport of combustible substances
4. Protect products against atmospheric oxygen when oxidation reactions would impair quality
5. Protect against atmospheric moisture, either to maintain product quality or to ensure optimal downstream processing, for example in grinding
6. Prevent health and safety hazards during maintenance of plants, apparatus and pipelines

A distinction is also made between continuous and intermittent applications:

Continuous applications:

- Blanketing of production processes to prevent fire and explosion and avoid oxidation (to safeguard quality)
- Inerting of solvent containers and transport equipment to prevent fire and explosion

Intermittent applications:

- Purging of pipelines
- Purging of tanks
- Inerting of filtering installations
- Inerting of silo installations
- Inerting of grinding plants
- Extinguishing of smouldering fires in silos

Inerting can also be carried out on a partial or complete basis. With partial inerting, the oxygen concentration is reduced to such a low level that the mixture ceases to be explosive. Complete inerting involves increasing the ratio of the inerting gas to the combustible material to such a level that even adding any amount of air cannot lead to an explosive mixture [6].

5. Inerting methods.

Different inerting techniques are available for different application challenges. With partial inerting (see Chapter 4), the objective is to reduce the concentration of oxygen in the mixture to such a level that it ceases to be explosive. The main methods employed are:

Purging

In this process, an inerting gas is introduced to an apparatus or pipeline in order to displace a process gas from it.

Blanketing

Blanketing helps to ensure that constant, inert conditions are maintained for a product, for example in a vessel. The objective is to prevent explosions, discolouration, polymerisation and other undesirable changes in quality. The operation is monitored through the flow rate and pressure of the inert gas stream and/or the oxygen level in the exhaust gas.

Sparging

Sparging involves passing finely dispersed gas bubbles through a liquid. This helps to improve mixing and increase the surface area for gas-liquid mass transfer. The technique is used in chemical and biological reactions, but also in stripping. Nitrogen is used for example to strip oxygen from oil, wastewater and other products.

There are several different purging methods:

Displacement purging

In displacement purging, inert gas is injected into an open apparatus to displace a dangerous or harmful gas. A slow flow rate will be maintained, e.g. $< 10 \text{ m/s}$. This method is used primarily when the H/D ratio* is high. The inert gas should ideally have a higher density than the gas to be displaced.

* H/D = Height/Diameter

Figure 9 shows how nitrogen is used for displacement purging of a vessel. The gas is supplied in a tanker. The liquid nitrogen (LIN) is vaporised in an evaporator, and the gaseous nitrogen (GAN) is then injected into the vessel. The nitrogen squeezes the atmosphere out of the vessel via the exhaust gas valve. The quantity of nitrogen required is relatively small, typically 1.2 times the capacity of the vessel.

Displacement purging (plug effect)

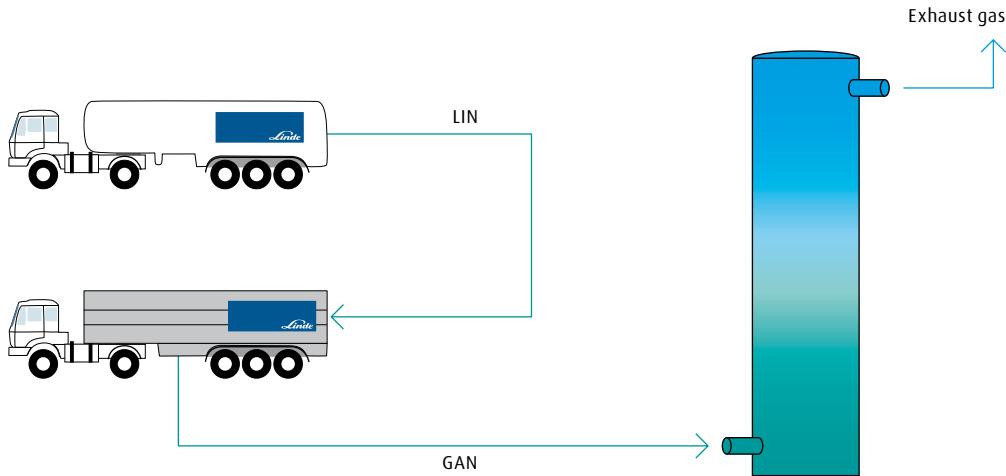


Figure 9: Displacement purging configuration

Dilution purging

Dilution purging involves injecting an inert gas to lower the concentration of a harmful or dangerous gas. This method is used when the apparatus has a lower H/D ratio. The amount of nitrogen required will be around 3.5 times the capacity of the vessel. The best way to achieve a good degree of mixing is to have wide spacing between the inlet and outlet ports and to choose an inert gas with a similar density to the harmful gas.

Dilution purging should not be used if there is dead space in the vessel, because this cannot normally be reached by the inert gas. The configuration in figure 10 shows how gaseous nitrogen is vaporised and injected into an apparatus with an open discharge valve. The diluted gas, composed of the harmful gas and nitrogen, is then discharged into the atmosphere or further processed.

Dilution purging

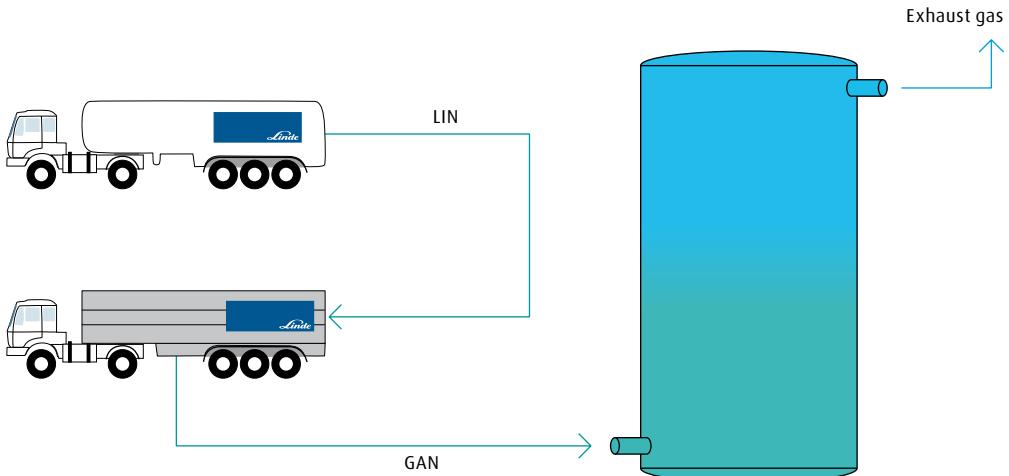


Figure 10: Dilution purging configuration

Pressure swing purging

In pressure swing purging, a closed apparatus is pressurised with an inert gas. When the gas is vented, the dangerous or harmful gas escapes. The process (closing – injection – opening – release) is continued until the desired concentration of the harmful gas in the apparatus is achieved. Pressure swing purging is used for example when the inlet and outlet ports are located close together. In addition, the apparatus must be a pressure vessel.

Vacuum purging

Vacuum purging involves extracting the harmful gas with a vacuum pump and then introducing an inert gas to the evacuated apparatus. This process is repeated until the desired concentration of harmful gas is reached.

Vacuum purging is particularly well suited for apparatus with several areas of dead space.

Inerting of pipelines

The following methods are used to expel process gases or liquids from a pipeline and to inert the system:

1. The process gas is forced from the pipeline by a plug of inert gas.
2. A pig driven by nitrogen pressure displaces the process gas. The pig can be made of solid material or foam.

Figure 11 shows a schematic view of both versions.

Inerting of pipelines

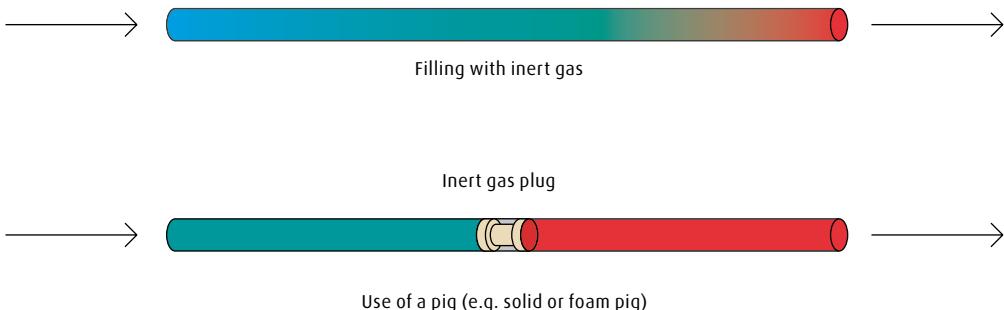


Figure 11: Methods for inerting of pipelines

The inerting time and the amount of inert gas required depend not only on the inerting method used, but also on the degree of mixing (e.g. plug flow, ideal mixing or bypass). Factors that influence the flow include the properties of the gas, the geometry of the space being inerted, the inlet and outlet port configuration and last, but not least, the flow velocity.

An example is the H/D ratio of the vessel. The following rule of thumb generally applies:

$H/D < 1$:

No plug flow → Dilution purging

$H/D > 10$:

Predominantly plug flow → Displacement purging

As the H/D ratio increases, the flow approaches plug flow and fewer vessel volume changes are needed. This also means that nitrogen consumption and inerting time decrease when the vessel volume is the same. Figure 12 shows the relationship between the exit concentration and the number of vessel volume changes with the inert gas at different H/D ratios.

If the aim of inerting is to achieve a very low concentration of the harmful gas, e.g. oxygen, high-purity nitrogen must be used. Figure 13 shows that if the maximum permissible oxygen concentration is very low (< 1%), the nitrogen purity must be higher than 99%. Using a higher purity makes it possible to reduce the number of vessel volume changes.

Exit concentration of gas to be displaced

— $H/D = 3$ — $H/D = 1$ — $H/D = 1/3$

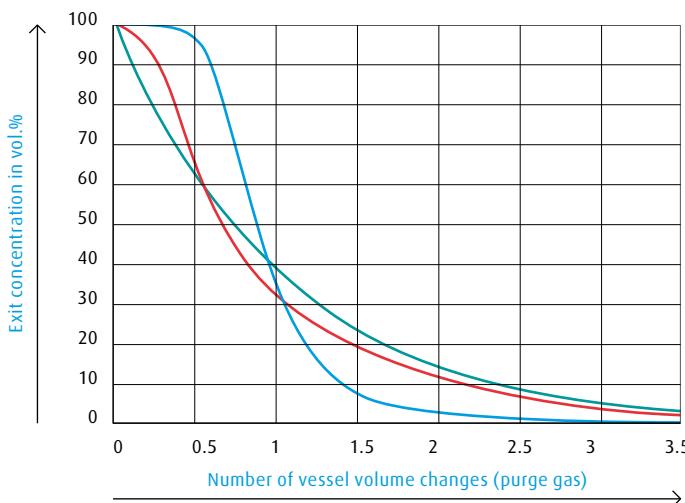


Figure 12: Exit concentration of gas to be displaced as a function of vessel volume changes at different H/D ratios

Max. permissible oxygen concentration

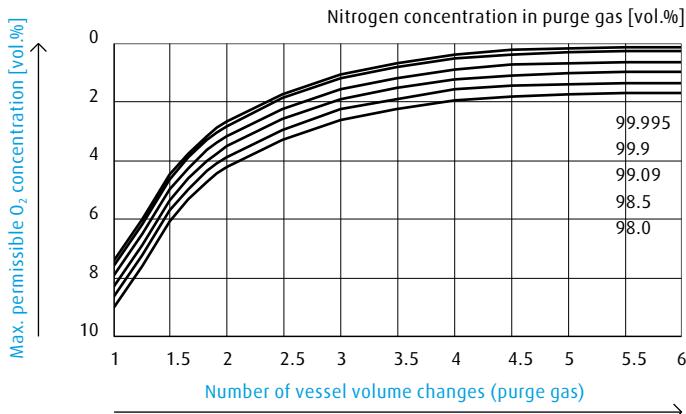


Figure 13: Maximum permissible oxygen concentration as a function of the number of vessel volume changes at different nitrogen purities [4]

The properties of carbon dioxide permit its use not only for inerting, but also for extinguishing smouldering fires in waste bunkers and silos containing organic material. A special nozzle (figure 14) has been developed for this purpose.

The nozzle ensures that the carbon dioxide is completely vaporised while remaining as cold as possible. In particular, this prevents the formation of CO₂ snow. The gas is blasted from the nozzle at a low velocity so that a stable layer can form above the bulk material.

In certain cases, as in the production of food supplements, argon is used instead of nitrogen as the inerting agent. The principal reason is that argon, being heavier than air, remains in the vessel when it is opened. Argon is therefore more effective at preventing contact between oxygen and the product. If an inert atmosphere needs to be maintained in a vessel in continuous operation, one of two options can be chosen:

- Constant purging with an inert gas or
- Introducing and maintaining slight inert gas overpressure

The second option should be chosen if feasible, because it requires less inert gas, which in turn means lower emissions.



Figure 14: Special nozzle for vaporising carbon dioxide [4]

6. Inerting equipment.

All inerting equipment and supporting installations must meet the strictest leak-proof standards. Equipment must be designed to prevent air from entering the system and explosive gases and vapours from exiting the system. Appropriate leak tests should therefore be carried out. The tests are often performed at a pressure of < 0.5 bar (abs.), i.e. following evacuation. Table 5 contains empirical values in relation to pressure.

The leak rate can be calculated using the following equation [7]:

$$L = 0,0072 \cdot \frac{\Delta p}{t} \cdot V_B$$

Whereby:

L = Leak rate in kg/h

Δp = Measured pressure increase in mbar

t = Measuring time in min

V_B = Vessel volume in m³

To meet the needs of the chemical industry, special equipment has been developed, built and successfully deployed for inerting. This equipment will be described in the following sections.

Table 5: Reference values for pressure increases per minute following evacuation to 0.5 bar (abs.)

$\Delta p/\Delta t$ in mbar/min	Application
> 0.2	Installation works under atmospheric pressure, e.g. driers
~0.5–1.0	Stirring tanks or similar closed systems
< 0.2	Tightly closed systems, e.g. vacuum distillation equipment at 1–10 bar (abs.)
0.0002–0.2	Installations for highly toxic substances



Figure 15: Simple measuring and metering station for the inerting of silos



Figure 16: Complex measuring and metering station for nitrogen intended for the inerting of vessels, mixers and reactors [4]

6.1 Measurement and metering stations

Figure 15 shows a simple measuring and metering station for nitrogen intended for the inerting of silos.

Figure 16 shows a complex measuring and metering station for nitrogen intended for the inerting of vessels, mixers and reactors. The key features of this station are its flow and pressure regulators and the corresponding indicator displays. For safety and portability reasons, the individual components are arranged in an enclosed and suitably ventilated cabinet.

6.2 Inert gas sluices

In fine and speciality chemicals manufacturing, some process stages – such as reactions in stirring tanks – involve not only liquids and gases but also solids. Certain situations can require the manual charging of solids. This means that air/oxygen will enter the vessel along with the bulk material. Inert gas sluices have been developed to reduce this admission of oxygen to a minimum. This helps to ensure safe handling during manual charging and prevent any secondary reactions such as oxidation.

The concept ensures that very little (atmospheric) oxygen is admitted when opening and manually charging vessels. For this, the charging port is purged with inert gas via inert gas sluices. The inert gas sluices can be permanent installations or positioned on the charging port as and when required for filling. A variety of different sluices are available and they can be easily adapted to any given usage scenario. A specially adapted inert gas regulator and supply system and, optionally, an oxygen analysis system ensure safe operation. Inert gas sluices can be deployed wherever manual charging of reactors or mixers is required and an inert atmosphere needs to be maintained, whether for safety and/or quality reasons.

The main advantages of inert gas sluices are:

- Admission of very little oxygen when the vessel is opened and charged
- Low inert gas consumption
- Easy to retrofit on the charging port of existing vessels
- Simplicity of routine operation
- Low investment and operating costs
- Design versatility allowing adaptation to specific applications

As a rule, nitrogen is used as the inert gas. The gas can be supplied from the plant's own network, from cylinder bundles or in liquid form, i.e. from a vacuum-insulated tank combined with an evaporator.

Figure 17 shows an inert gas sluice integrated into the charging port of a mixer. To adjust the height, the (threaded) bolts of the cover hinge merely need to be extended.

A schematic view of an inert gas sluice is shown in figure 19. The inert gas is injected at the top and flows inside the hollow body of the lock in a downwards direction. It emerges in the main body of the interior in the direction of the sluice's central axis.



Figure 17: Inert gas sluice (shown here: N₂LOCK™ from Linde)



Figure 18: Nozzles for injecting liquid nitrogen into a gas stream [4]

Preventing the admission of (atmospheric) oxygen when opening a vessel

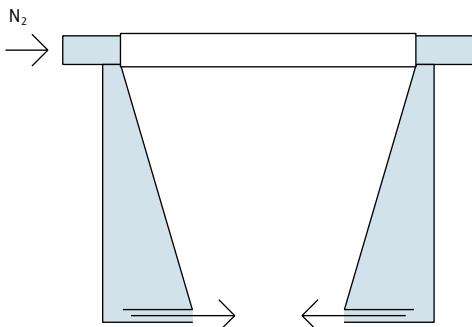


Figure 19: Design and function of an inert gas sluice N₂

Change in O₂ concentration in vessel

— sluice inactive — sluice active

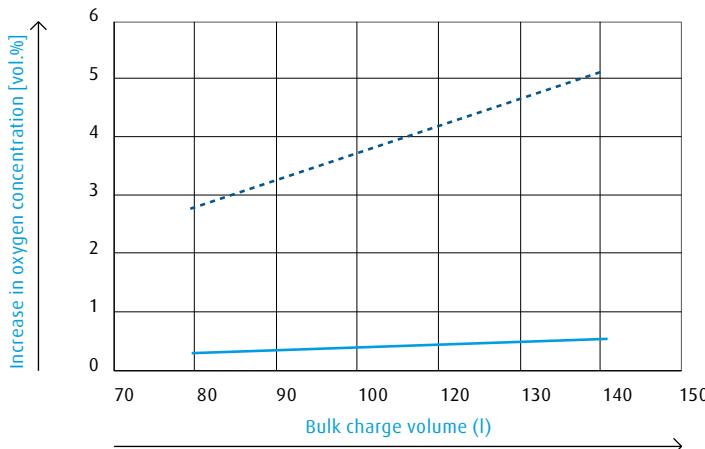


Figure 20: Change in oxygen concentration in vessel as a function of bulk charge volume when sluice is active and inactive

Using an inert gas sluice when manually charging a vessel makes it possible to keep the oxygen concentration in the vessel at the desired low value.

Figure 20 compares two charging operations with the same vessel (volume approx. 2.3 m³; charging port approx. 500 mm; O₂ concentration prior to charging approx. 2% by vol.). There is a linear dependency between the increase in O₂ concentration and the bulk charge volume. By activating the inert gas sluice pressurised with nitrogen (consumption approx. 5 to 20 Nm³/h depending on type), the oxygen concentration level can be significantly reduced, i.e. the inert gas sluice effectively reduces the admission of air/oxygen when the material is being charged.

6.3. Nozzles for injecting liquid nitrogen into a gas stream

Using special nozzles, liquid nitrogen can be distributed in piping – over a wide range of flow rates – in such a way that the mixing zone is short and virtually no liquid nitrogen reaches the pipe wall or downstream apparatus. The danger of embrittling the material of the pipeline or apparatus is greatly reduced as a consequence. Figure 18 shows nozzles used for injecting liquid nitrogen into a stream of gas flowing in a pipe to a reactor or another apparatus.

6.4 Inert gas blanketing in tanks

Inert gas blanketing is used for oxygen-sensitive liquids in tanks to protect product quality or for safety reasons. The process involves “blanketing” the headspace above the liquid level in the tank with an inert gas atmosphere, which is maintained even during filling and emptying operations with a specially designed system incorporating valves.

A constant overpressure of a few millibars is automatically maintained inside the tank while it is

being used. Figure 21 shows a schematic view of an inert gas blanketing system that automatically ensures that the headspace above the liquid is continuously filled with inert gas, regardless of whether the tank is being filled or emptied.

Such inert gas blanketing systems often work on a purely mechanical basis and usually do not require any auxiliary electrical or pneumatic power. They can easily be installed as a complete package, tailored for the tank's specific requirements (see figure 22).

Figure 21: Automatic system for inert gas blanketing in tanks

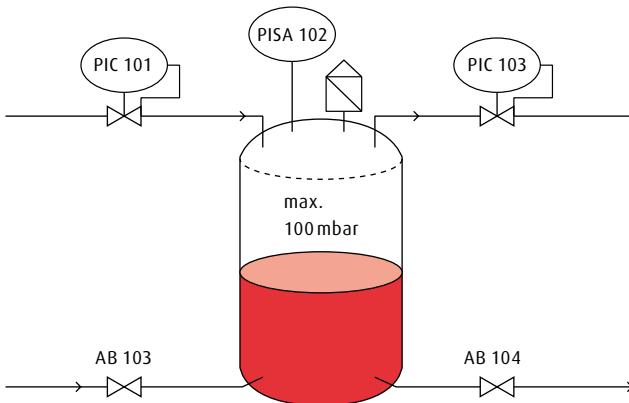




Figure 22: Inert gas blanketing system with pressure reducing valve, back pressure regulator and safety valve
(shown here: GAXINERTER™ from Linde)

7. Software for inerting.

Inerting is one of the most common processes used in the chemical industry. An estimated 60–70% of the nitrogen consumed in the chemical industry is used for this purpose. To provide additional support for the application engineers who advise customers on-site, software was developed in the 1980s to create ignition range diagrams for flammable gas mixtures. This software has undergone continuous development over the years, with several modules added. Linde's application engineers can now build on a package of supporting programmes to help their customers calculate safety thresholds, the amount of nitrogen required, or the purging time. These support tools have proven their worth time and again in the chemical industry. The following sections will provide brief descriptions of the two main programmes, the Linde Safety System™ and PAM – Process Application Management.

7.1. Linde Safety System™

The Linde Safety System™ is a programme to compute flammability diagrams. The data is drawn from the Design Institute for Physical Properties (DIPPR) database. The DIPPR is a technical society of the American Institute of Chemical Engineers AIChE. DIPPR is one of the world's best and most well-known sources for critically evaluated thermodynamic property data. The database contains thermodynamic constants and temperature-dependent properties (in the form of equation parameters) for approx. 2,000 industrially relevant substances.

With the Linde Safety System application, engineers can create a flammability diagram (safety triangle) for the substance or mixture found at the customer's site (provided the data on the pure substances is contained in the DIPPR database). The key features of the programme are as follows:

- Flammability diagrams can be calculated for substance mixtures containing up to 99 (flammable) components
- Freely selectable temperature range (dependent on substance properties of the components)
- Choice of inert gas (N_2 , CO_2 , Ar, He or H_2O)
- Variable oxygen concentration (1 to 100 vol.%)
- On-screen preview and print-out possible
- Cannot be used for dust
- Values are always calculated for pressure of 1 bar(a)
- Temperatures higher than the auto-ignition temperature of individual components cannot be calculated

Figure 23 shows a flammability diagram calculated with the Linde Safety System.

7.2. PAM – Process Application Management

With the current programme module, calculations can be made for inerting processes like dilution purging and pressure swing purging. For optimum support of each application, the user can select different geometrical parameters for the vessel or tank. Other parameters include pressure limits,

the available inert gas volume flow rate and local and process-related conditions.

If the user enters data that is not consistent or plausible in view of previous entries, warnings are displayed, or else the user cannot continue until the value entered has been changed. This prevents scenarios whereby, for example, excessively high pressure builds up because the inert gas volume flow rate in the vessel is too high and the outlet cross-section of the ventilation opening or pipe is too small.

The PAM module is linked with the SST (Linde Safety System) module. During data entry, the flammability diagram (based on the DIPPR pure substance data) is calculated in the SST module and the results are fed to the PAM module.

The output which the application engineer receives contains data on, for instance, the inert gas requirement, the purging time, and the number and ultimate pressure of inert gas purge cycles (for pressure swing purging). This data will be used to prepare for and carry out the inerting operation. Figure 24 shows a sample data calculation.

Safety system – flammability triangle

At 25 °C and 1 bar (a) for mixture (fuel)

[L] Lower flammability limit (3.3 vol.% fuel), [U] Upper flammability limit (14.8 vol.% fuel), [S] Min. O₂ for flammability (9.2 vol.% oxygen, 3.7 vol.% fuel), [C] Start up (max. 9.5 vol.% oxygen), [B] Shut down (max. 6.5 vol.% oxygen)

Inert gas: Nitrogen. Fuel mixture [vol.%]: methane [75], propane [15], isobutane [10]

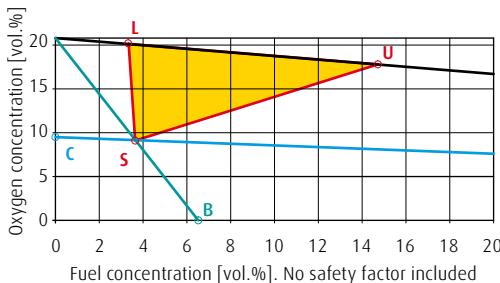


Figure 23: Safety triangle calculated using the Linde Safety System

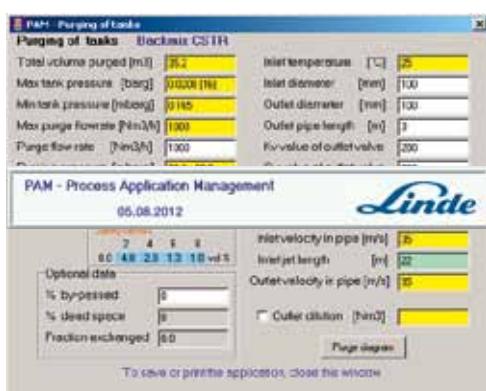


Figure 24: Sample data calculation with PAM

8. Calculation equations and examples.

Chapter 5 described the various inerting techniques in detail. This chapter will compile the calculation equations for each method and provide examples to describe their use.

8.1 Dilution purging

According to the reference source [7], the following calculation equations can be used for this method:

Number of volume changes:

$$i = \ln (c_a/c_e) \quad (\text{EQ1})$$

Volume of inert gas required:

$$V_N = i \cdot V_B \quad (\text{EQ2})$$

Whereby:

i = Volume change

C_a = Initial concentration

C_e = Final concentration

V_N = Volume of inert gas

V_B = Volume of vessel

Sample calculation:

A vessel is filled with methane. Its volume is 2,000 m³. The initial concentration is 100 vol.%. After inerting, the final concentration should be 4 vol.%. The dilution purging method is to be used. How many volume changes are needed? How much nitrogen will be needed?

Calculation:

Vessel volume: 2,000 m³

Initial concentration: 100 vol.%

Target final concentration: 4 vol.%

$$i = \ln (100/4) = \ln 25 = 3.22$$

$$V_N = 3.22 \cdot 2,000 = 6,440 \text{ m}^3$$

To achieve the final concentration of 4 vol.%, 3.22 volume changes are needed. The nitrogen volume required is 6,440 m³ minimum.

8.2 Pressure swing purging

In pressure swing purging, a distinction is made between vacuum purging and overpressure purging. One of the main objectives of pressure swing purging is to arrive at a certain concentration of a dangerous or harmful substance, e.g. oxygen. The residual concentration of the harmful substance can be calculated using the following equation [8]:

$$C_{SR} = \left(\frac{p_1}{p_2} \right)^n \cdot (C_{SG} - C_{SI}) + C_{SI} \quad (\text{EQ3})$$

Whereby:

C_{SR} = Residual concentration of harmful substance

C_{SG} = Concentration of harmful substance in mixture

C_{SI} = Concentration of harmful substance in inert gas

n = Number of pressure swings

p_1 = Pressure 1 (prior to inerting)

p_2 = Pressure 2 (following inerting)

8.2.1 Vacuum purging

The effective inert gas requirement [7,8] is calculated as follows:

$$V_N = V_B \cdot f \cdot n \quad (\text{EQ4})$$

Whereby:

V_N = Inert gas requirement in m^3

V_B = Vessel volume in m^3

f = Pressure change ratio

n = Number of pressure swings

Number of volume changes:

$$i = (\ln c_a - \ln c_e) / (\ln p_2 - \ln p_1) \quad (\text{EQ6})$$

Volume of nitrogen:

$$V_N = V_B \cdot i \cdot (p_2 - p_1) / p_0$$

The pressure change ratio equation is as follows:

$$f = 1 - \frac{p_1}{p_2}, \frac{p_1}{p_2} < 1 \quad (\text{EQ5})$$

f = Pressure change ratio

p_1 = Pressure prior to inerting

p_2 = Pressure following inerting

Whereby:

c_a = Initial concentration

c_e = Final concentration

p_1 = Pressure after pressure increase

p_2 = Pressure after pressure release

p_0 = Pressure prior to pressurisation

V_B = Volume of vessel

i = Volume change

Sample calculation:

→ Calculation of residual concentration [7,8]

The pressure is reduced from atmospheric pressure to 0.5 bar. The oxygen concentration in the mixture is 21 vol.% and 0.5 vol.% in the inert gas. Two pressure swings are carried out. From this, the following residual concentration of oxygen can be calculated according to the equation (EQ3) above:

$$c_{\text{OR}} = (0.5/1.0)^2 \cdot (21-0.5) + 0.5 = 5.62 \text{ vol.\%}$$

→ Calculation of inert gas requirement [7]

How much inert gas is needed to reach a final concentration of 5.62 vol.% if the vessel has a volume of 10 m^3 ?

The equations (EQ4) and (EQ5) show that:

$$V_N = 10 \cdot \left[1 - \frac{0.5}{1.0} \right] 2 = 10 \text{ m}^3$$

In this case, 10 m^3 of nitrogen is required.

Sample calculation:

A vessel is filled with methane. Its volume is $2,000 \text{ m}^3$. The initial concentration is 100 vol.%. After inerting, the final concentration should be 4% by volume. The overpressure purging method is to be used. The pressure following the pressure increase is 2 bar; following the pressure release it is 1 bar; and prior to pressurisation it is 1 bar. How many volume changes are needed? How much inert gas will be needed?

Calculation:

Vessel volume: $2,000 \text{ m}^3$

Initial concentration: 100 vol.%

Desired final concentration: 4 vol.%

Number of pressure swings:

$$i = (\ln 100 - \ln 4) / (\ln 2 - \ln 1) = 4.6$$

Volume of inert gas required:

$$V_N = 2,000 \cdot 4.6 \cdot (2-1) / 1 = 9,200 \text{ m}^3$$

With pressure swing purging, 4.6 pressure swings and $9,200 \text{ m}^3$ of inert gas are needed.

8.2.2 Overpressure purging

The following equations are used for overpressure purging:

9. Safety through inerting.

9.1 General

One of the main reasons for inerting is to prevent explosions. The following factors are needed for an explosion to occur: a flammable substance, oxygen and a source of ignition. The risk of explosion can be averted by avoiding the formation of an explosive atmosphere, reducing oxygen concentration through the use of inert gas and excluding ignition sources.

The following sections will describe how the formation of an explosive mixture can be avoided through the use of inert gas. The main terms used in connection with explosion protection are explained in Appendix 2.

Sample triangular diagram

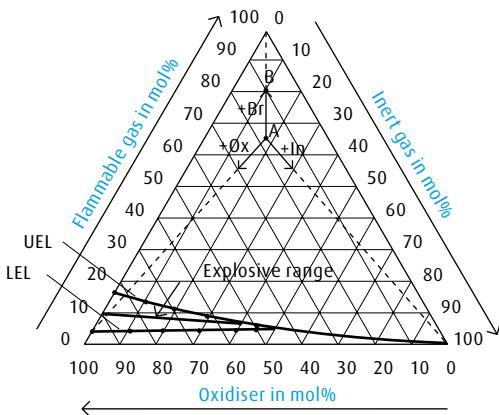


Figure 25: Triangular diagram showing explosive range of a flammable gas [9]. LEL is the lower explosive limit and UEL the upper explosive limit.

9.2 Explosion diagrams

Determining the approach to take and conditions to apply when inerting requires familiarity with the explosive range. This can be gained by examining explosion diagrams. Triangular diagrams are the most commonly used format. The advantage of this type of diagram is that the substance quantities of the individual components are shown. Figure 25 shows a sample diagram.

To aid understanding, the diagram will be explained in detail based on the description in [9]:

- A is a substance mixture comprised of 65 mol% flammable gas, 17.5 mol% oxidising agent (also known as the oxidiser) and 17.5 mol% inert gas. The values are identified by translating the coordinate lines to point A and reading the values on the corresponding coordinates of the triangle. Since substance mixture A lies outside of the explosive range, there is no risk of explosion.
- The explosive range is arrived at by entering the experimental values obtained and through graphical or mathematical interpolation. If the composition of the gas mixture lies in the explosive range, then it is explosive. This means that the presence of an ignition source will cause dangerous reactions. But what about mixtures with a composition that puts them on the borderline? According to German and EU regulations, these compositions do not cause dangerous reactions.

Another way to present the explosive range of a flammable gas in graphic form is to use cartesian coordinates. Figure 26 provides an example.

The disadvantage of this type of diagram is that it does not show the third component. This can, however, be calculated as follows:

$$X_{\text{Oxidiser}} = (100 - X_{\text{Flammable gas}} - X_{\text{Inert gas}})$$

The advantage here is that a spreadsheet programme can be used. There are no mixtures in the shaded area because the sum of the individual components would produce mixtures exceeding 100 mol%.

For "A" and the "explosive range", see the explanations for the triangular diagram. A number of different methods can be used to determine the explosive limits [9]:

- Method according to DIN 51649-1/DIN EN 1839
- Method according to ASTM E 681-04
- Method according to prEN 1839 (tube and bomb methods)

These methods are carried out at atmospheric pressure and a maximum temperature of 200 °C. In all methods, defined gas mixtures are produced and subjected to ignition attempts. The differences between the measuring methods lie in the ignition vessels, the ignition sources, the criteria for ignition, the incrementation applied and the number of check tests. As a result, different explosive limits will be found depending on the method used. More information can be found in the reference sources, such as [9].

Explosive range of a flammable gas

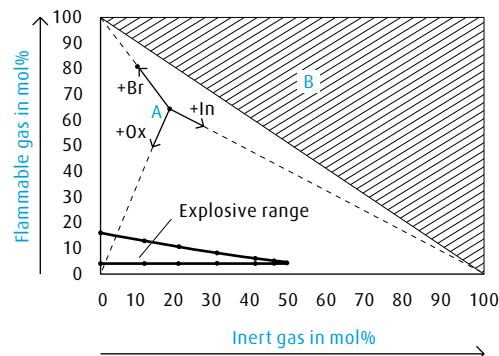


Figure 26: Explosive range of a flammable gas in the cartesian coordinates system [9]

The explosive limits are pressure- and temperature-dependent. The higher the temperature, the wider the explosive range. Table 6 shows some examples of this. When the initial pressure rises, the explosive range likewise expands. This leads to only a slight change in the lower explosive limit, but the upper explosive limit increases by a significant factor, as seen in table 7.

The ignition power also influences explosive limits, as table 8 demonstrates. In the tables, LEL stands for lower and UEL upper explosive limit.

Additional explosive limits and ignition temperatures are indicated in Appendix 1.

Table 6: Influence of temperature on the lower and upper explosive limits in air at 1 bar

Gas	20 °C		400 °C	
	LEL in vol.%	UEL in vol.%	LEL in vol.%	UEL in vol.%
Hydrogen	4.0	75.6	1.3	85.4
Carbon monoxide	12.5	74.0	8.0	84.7
Methane	4.4	17.8	2.8	34.4

Table 7: Influence of pressure on the lower and upper explosive limits in air at 20 °C

Gas	1 bar		100 bar	
	LEL in vol.%	UEL in vol.%	LEL in vol.%	UEL in vol.%
Methane	4.4	17.8	4.3	46.6

Table 8: Influence of ignition power on the lower and upper explosive limits in air at 20 °C and 1 bar

Gas	1 Joule		10,000 Joules	
	LEL in vol.%	UEL in vol.%	LEL in vol.%	UEL in vol.%
Hydrogen	4.9	13.8	3.6	17.5

9.3. Limiting oxygen concentrations

From a safety standpoint, the limiting oxygen concentration (LOC) is a key criterion for inerting. For a specific fuel/air/inert gas mixture, this parameter is the highest concentration of oxygen at which no explosion takes place by itself. The LOC is a specific value which must be determined by experiment.

Mathematical correlations for this do not exist. The values for simple substance mixtures have been compiled in tables.

The maximum permissible oxygen concentration is obtained by deducting a safe concentration margin from the experimentally determined limiting oxygen concentration. The explosion protection rules BGR 104 [6] state the following

about determining the safe concentration margin: "The safety margin between the experimentally determined limiting oxygen concentration and the maximum permissible oxygen concentration must be specified taking account of spatial and temporal variations resulting from operational factors and malfunctions and of the delay between triggering of protective measures and their becoming effective." Table 9 shows selected examples of flammable gases and vapours with nitrogen and carbon dioxide as inerting agents. The LOC values for carbon dioxide are significantly higher in some cases. The values also depend on the temperature. For flammable gases and vapours, the rule of thumb is that the limiting oxygen concentration falls by 0.5 to 1.0 vol.% when the temperature rises by 100 °C.

Table 9: Selected LOC values of flammable gases and vapours with nitrogen and carbon dioxide as inerting agents [10]

Fuel	LOC in vol.-%	LOC in vol.-%
	Nitrogen/air	Carbon dioxide/air
Benzene	11.2	13.9
Butadiene	10.4	13.0
Cyclopropane	11.7	13.9
Ethylene	10.0	11.7
Hexane	12.1	14.5
Methane	12.0	14.5
Propane	11.5	14.5
Hydrogen	5.0	5.2
Methanol	10.0	12.0

Limiting oxygen concentrations for various types of dust have also been determined for inerting dust/air mixtures. The fineness of the dust was a factor taken into consideration. Table 10 contains some examples for inerting with nitrogen.

The values are higher here, too, when carbon dioxide is used as inerting agent instead of nitrogen. The limiting oxygen concentration does not just depend on the inerting gas, but also on the pressure and temperature. The LOC values decrease as the temperature and pressure increase. As a general rule for combustible types of dust, when the temperature increases by 100 °C, the LOC value decreases by approx. 1.6 vol.% [1].

With light alloy dusts, noble gases are often used for inerting because there is a risk of reaction with carbon dioxide or nitrogen. Combustible dust deposits can give rise to glowing and smouldering fires.

To prevent dust explosions in such situations, the oxygen concentrations chosen must be significantly lower than the LOC values. These must be determined separately [6].

With mixtures of gaseous and dusty mixtures, the maximum permissible oxygen concentration must be determined using the component with the lowest limiting oxygen concentration.

Table 10: LOC values of selected dust types when inerting dust/air mixtures at 20 °C and 1 bar [11]

Type of dust	Fineness (median) in µm	Limiting oxygen concentration in vol.% in gaseous phase
Aluminium	22	5
Lignite	63	12
Cellulose	25	15
Urea	<10	10
Wood	27	10
Hops	500	17
Rubber	95	11
Methyl cellulose	70	10
Wheat flour	60	11

The LOC cannot itself be used for process control because of uncertain variables like:

- Accuracy of the LOC values
- Fluctuations in pressure and temperature during the process
- Stability of the process
- Speed control system reacts to process changes
- Accuracy of the oxygen measurement

Various levels are therefore determined for process control. Cunliff [12] has proposed four levels, for instance:

- LOC
- Maximum permissible oxygen concentration
- First alarm level
- Normal operating conditions

Table 10 also indicates that working with many hydrocarbons is often safe when the oxygen concentration is lower than 10% and a safety margin of e.g. 2 vol.% is assumed. However, this is only the case at atmospheric pressure and ambient temperature.

As a general rule, when the temperature increases by 100 °C, the LOC decreases by 0.5–1.0 vol.%.

In apparatus in which the oxygen concentration is continuously measured, a safety margin of 2 vol.% is often applied. If the concentration is not continuously measured, the permissible oxygen concentration should be 60% of the LOC or lower. This precaution should provide a sufficient safety margin on the one hand while also preventing false alarms, which could for example result in shutdown of the plant.

10. Hazards for personnel handling nitrogen and carbon dioxide.

Guaranteeing safety is paramount when inerting. The following hazards in particular must therefore be addressed when using inert gases:

Asphyxiation

When it is necessary for personnel to work in a partly inerted environment, for example during cleaning, the oxygen level must be kept at a minimum of 15 vol.%. Table 11 provides further information.

Contact with cryogenic liquid nitrogen leads to cold burns and frostbite. Protective clothing, particularly safety gloves and safety glasses, must therefore be worn when handling liquid nitrogen.

In light of the low temperatures involved, liquid nitrogen (LIN) can diminish the ductility and

toughness of some materials, such as carbon steel, so that they become embrittled and may fracture. LIN should not therefore be used for such materials. Suitable materials include stainless steel, copper and aluminium. Carbon dioxide has certain characteristics that differentiate it from nitrogen and argon. The CO₂ concentration in air is around 0.03 vol.%. At higher concentrations, the human body cannot differentiate between metabolically produced CO₂ and the CO₂ present in the atmosphere. The initial effect is faster breathing. The effects felt at higher concentrations are detailed in table 12. Inert gases must therefore be handled with extreme care, especially as they are for the most part colourless and odourless.

Table 11: Effects of atmospheric oxygen concentration on humans and the flammability of materials, see also [1]

Oxygen level in apparatus (vol.%)	Effects on human body	Effects on flammability of materials
4-6	Coma in 40 s, convulsions, death	Non-flammable
6-8	Death after 8 min at the latest	Non-flammable
8-10	Danger of death, unconsciousness, nausea, inability to move	Non-flammable
10-12	Poor judgement and pain perception, blue lips	Non-flammable
12-14	Fatigue, increased respiration and pulse rate, impaired judgement	Low flammability
15-19	First signs of oxygen deficiency, decreased ability to work	Low flammability
21	None	None

11. Monitoring of inerting.

Regardless of the method used for inerting, monitoring by taking careful measurements is essential. Variables that should be measured and monitored include oxygen concentration, inert gas concentration, and mass flows of inert gas and flammable materials/oxygen. The use of monitoring equipment, such as oxygen analysers, can help to improve safety, optimise inert gas consumption and reduce emissions to a minimum. Systems to measure oxygen concentration must fulfil the following important criteria:

The sensor must be adapted to the particular conditions/risk factors of the measuring point.

Such conditions/factors might include:

- Do flow and pressure fluctuations occur?
- How fast should the reaction times be?

The sensor must work reliably and be easy to calibrate. The time delay must not be longer than 60 s [12].

Measuring accuracy of ± 1 vol.% [13] is sufficient.

Typical varieties of oxygen analysers are:

- Electrochemical cell
- Paramagnetic sensor
- Zirconium oxide sensor

Table 12: Effects of carbon dioxide inhalation [1]

Carbon dioxide in vol.%	Effects of CO ₂ inhalation
1	Breathing rate increases slightly.
2	Breathing rate increases by up to 50% of normal level. Prolonged inhalation leads to headache and fatigue.
3	Breathing increases to twice the normal rate and becomes laboured. Slight narcotic effect. Impaired hearing, headache, increased blood pressure and pulse rate.
4-5	Breathing increases to approx. four times the normal rate. Symptoms of intoxication become evident and slight choking may be felt.
5-10	Characteristic pungent odour is noticeable. Very laboured breathing, headache, visual impairment and ringing in the ears. Judgement may be impaired, followed within minutes by loss of consciousness.
50-100	A concentration in excess of 10% rapidly leads to fainting. Prolonged exposure to high concentrations may eventually result in death from asphyxiation.

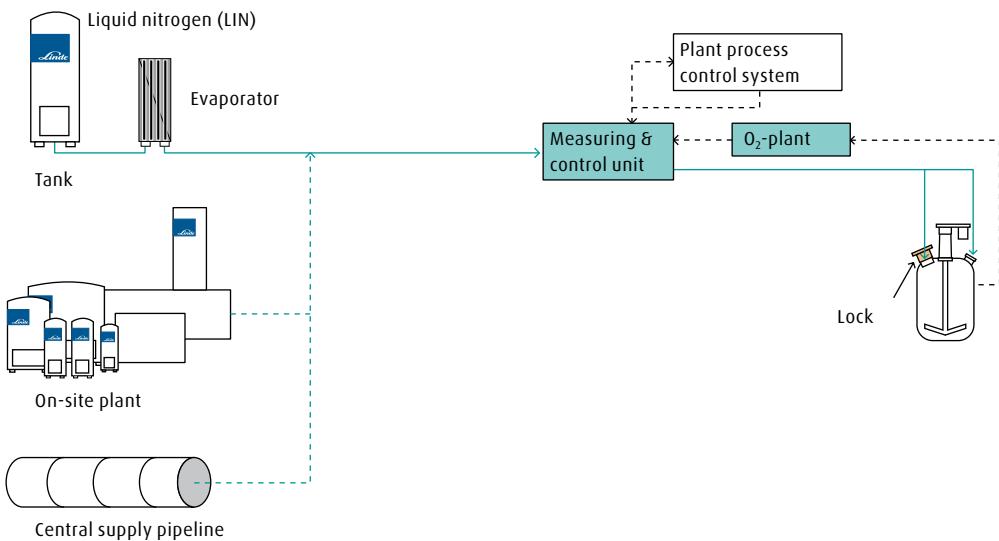
12. Examples.

12.1. Supplying nitrogen to a reactor during startup and shutdown and when charging a solid

Figure 27 illustrates how nitrogen can be supplied to a reactor or mixer. There are three options for nitrogen delivery. The system includes a measurement and control unit, an oxygen analyser for

monitoring the oxygen level in the headspace of the apparatus, and an inert gas lock for charging. In an example drawn from synthetic fibre manufacturing, molten polyamide is produced using nitrogen as inert gas. The reason is that molten polymer suffers from marked oxidation by oxygen.

Figure 27: Supply of nitrogen to a reactor



12.2. Industrial services

The chemical industry often requires large volumes of nitrogen for tasks associated with preparing for and executing repeat shutdowns. Nitrogen is used to inert the system during shutdown and cooling, in pressure testing, in drying (of catalysts in particular) and in pre-heating under inert conditions preparatory to startup. An example is the shutdown of an ethylene cracker, where the following conditions were needed:

- Nitrogen consumption: 1,000–6,000 Nm³/h
- Pressure: 9–40 bar
- Temperature: ambient to +200 °C



Figure 28: Use of liquid nitrogen to cool down a reactor

Figure 28 shows an inerting and cool down operation at a reactor. Inerting and accelerated cool-down of a fixed bed reactor with liquid nitrogen leads to:

- Accelerated inerting of the catalyst
- Shorter cool-down time
- Saving in cost because piping does not have to be reconfigured

Figure 29 shows the technical configuration for a reactor cool-down through the controlled injection of liquid nitrogen in the recycling gas flow of the reactor.

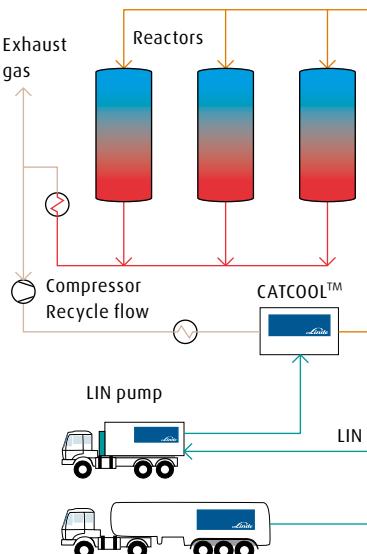


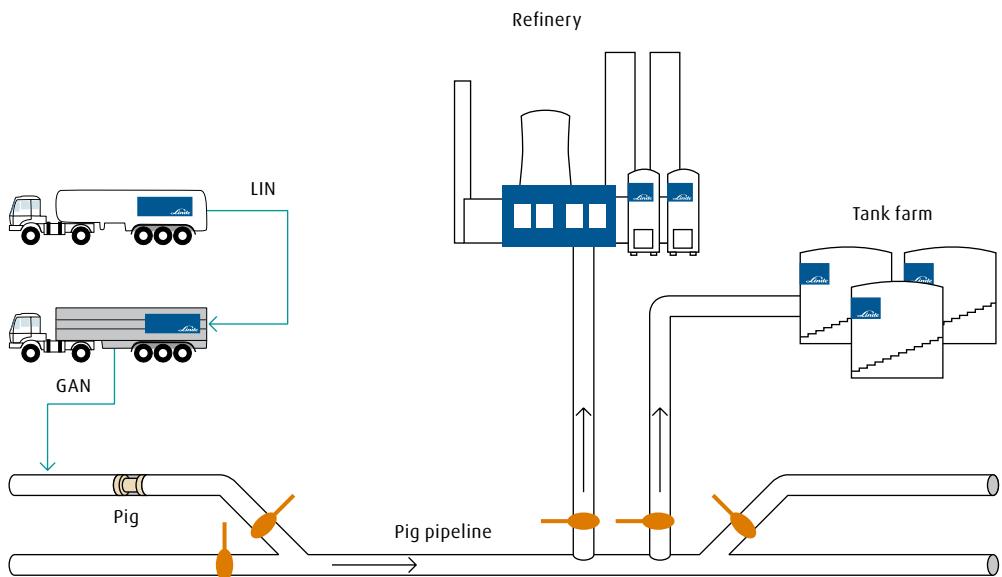
Figure 29: Technical configuration for accelerated cool-down of three reactors

Pigging and other pipeline maintenance operations are also often carried out under nitrogen inerting.

Nitrogen pushes a pig through a pipeline or piping system (figure 30). The advantages of using nitrogen to move the pig include:

- Inerting
- Anti-corrosion action of dry gas
- Wide range of volume flow rates, pressures and temperatures

Figure 30: Pipeline pigging using nitrogen



13. Treatment of exhaust gas.

Exhaust gases from inerting and cleaning operations are often contaminated with hydrocarbons. These must be removed before the gas is vented into the atmosphere. This can be done by means of cryocondensation, an adsorber or a combustion plant.

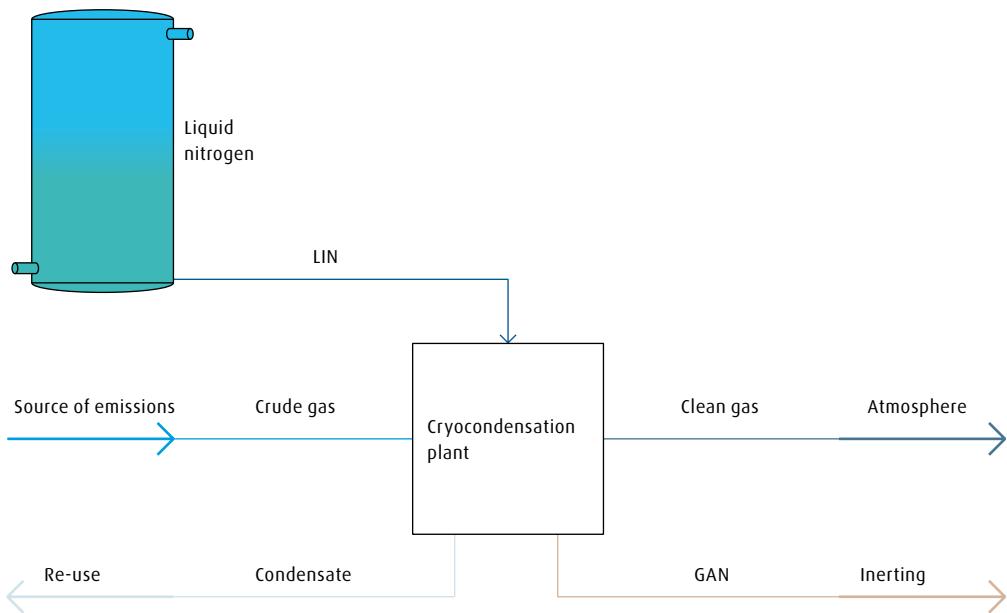
Cryocondensation [14] can be especially advantageous because the cryogenic effects of the nitrogen – used for inerting – is utilised. Other advantages include:

- No auxiliary materials, as is the case in adsorption for example
- Low investment costs
- Small number of moving parts

- Flexible solvent loading
- Fast startup and shutdown of plant
- Simple and fully automatic operation

The temperature required to undercut the dew point or comply with the statutory exhaust emission standards can easily be set and controlled using liquid nitrogen (-196°C at 1 bar) as the cooling agent. Cryocondensation thus enables temperatures of -150°C and lower, which will be required in some cases. Figure 31 shows how cryocondensation can be integrated into the process for cleaning an exhaust gas flow.

Figure 31: Cryocondensation block diagram [15]



Cryocondensation can be used to clean exhaust gas flow rates of up to 1,000 Nm³/h and different contaminant loads, e.g. solvents.

Both standard units (figure 32) and customised solutions are available. These units can also be implemented as mobile systems.



Figure 32: Standard cryocondensation units for exhaust gas flow rates of 50, 150 and 500 Nm³/h [15]

Customised cryocondensation units are available for higher throughputs and more complex separation tasks (figure 33). Figure 34 shows a diagrammatic view of a customised cryocondensation unit. It consists of three heat exchangers and enables effective recovery of resources.

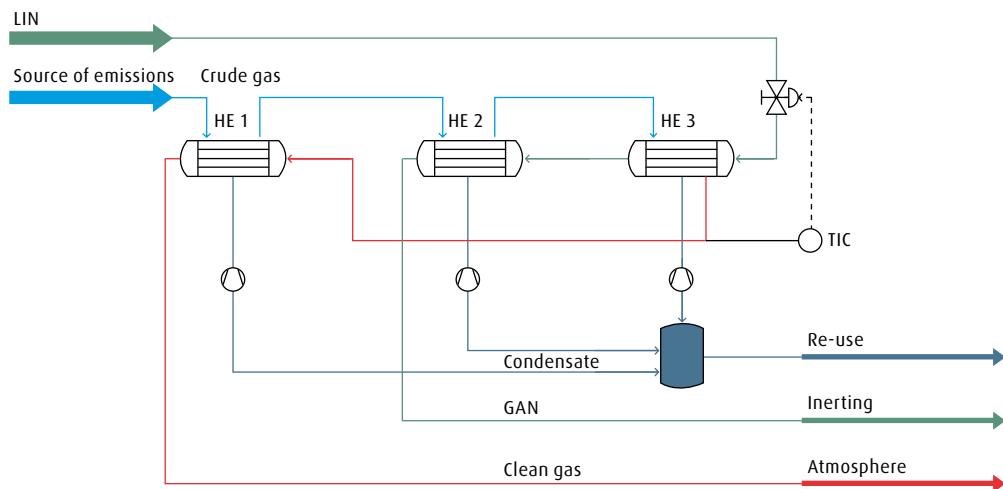
A sample application is described below:

After an air separation unit was purged with perchloroethylene, the atmosphere within the unit was saturated with gaseous perchloroethylene. The perchloroethylene atmosphere was to be eliminated by purging with nitrogen. The nitrogen flow then contained perchloroethylene, which was removed through cryocondensation. A CIRRUS® M50 unit, shown in figure 32, was used for this purpose. The residual load of the nitrogen flow was 10 ppm, which corresponded to a load of 80 mg/m³ [15].



Figure 33: CIRRUS CD™, cryocondensation unit

Figure 34: Flow diagram for three-stage cryocondensation [15]



14. Services provided by gases companies.

When it comes to inerting, chemical companies can often benefit from partnering with a gases supplier, which will invariably have a wealth of experience in different inerting processes and methods. Gas suppliers can offer the following services:

- Application-specific advice on the optimal supply mode, safety and hardware specifications
- Performance of safety and cost-efficiency analyses
- Tests at customer's site or pilot plant to check effectiveness of inert gas sluices, for instance
- Leasing or fabrication and delivery of inerting hardware
- Supply of required quantities of inert gas



15. Abbreviations.

Abbreviation	Measurement	Unit
c_a	Initial concentration	Vol.%, g/m ³
c_e	Final concentration	Vol.%, g/m ³
c_{OR}	Residual concentration of oxygen	Vol.%, g/m ³
c_{SG}	Concentration of harmful substance in mixture	Vol.%, g/m ³
c_{SI}	Concentration of harmful substance in inert gas	Vol.%, g/m ³
c_{SR}	Residual concentration of harmful substance	Vol.%, g/m ³
D	Diameter	m
Δp	Pressure change	bar
f	Pressure change ratio	-
H	Height	m
i	Number of volume changes	-
L	Leak rate	m ³
LIN	Liquid nitrogen	
LOC	Limiting oxygen concentration	Vol.%, g/m ³
n	Number of pressure swings	-
UEL	Upper explosive limit	Vol.%, g/m ³
p_0	Pressure prior to pressurisation	bar
p_1	Pressure at state 1	bar
p_2	Pressure at state 2	bar
t	Time	s, min, h
LEL	Lower explosive limit	Vol.%, g/m ³
V_B	Vessel volume	m ³
V_N	Inert gas volume	m ³
x	Molar fraction	Mol.%

16. References.

- [1] AICHE, 38th Annual Loss Prevention Symposium, April 25-29, 2004, New Orleans, Louisiana.
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Appendix 1: Explosive limits and ignition temperatures for selected flammable gases and vapours.

Explosive substance	Explosive limits in air		Ignition temperature in °C
	in vol.%	in g/m ³	
Acetaldehyde	4.0–57.0	73–1040	140
Acetone	2.5–13.0	60–130	540
Acetylene	2.4–83	15–30.2	305
Ammonia	15.0–30.2	105–215	630
Aniline	1.2–11.0	48–425	425
Benzaldehyde	1.4	60	190
Benzene	1.2–8.0	39–270	555
Prussic acid (hydrogen cyanide)	5.4–46.6	60–520	535
Butadiene	1.4–16.3	31–365	415
n-butane	1.5–8.5	37–210	365
tert-Butanol	1.4–10.0	43–310	340
Chlorobenzene	1.3–7.0	60–330	(590)
Diethyl ether	1.7–36	50–1100	180
Dioxane	1.9–22.5	70–820	375
Acetic acid	4.0–17.0	100–340	485
Acetic anhydride	2.0–10.2	85–430	330
Ethane	3.0–12.5	37–155	515
Ethanol	3.5–15.0	67–290	425
Ethyl acetate	2.1–11.5	75–420	460
Ethyl bromide	6.7–11.3	300–510	510
Ethyl chloride	3.6–14.8	95–400	510
Ethylene	2.7–28.5	31–330	425
Ethylene glycol	3.2–53.0	80–1320	410
Ethylene oxide	2.6–100	47–1820	440
Carbon dioxide	12.5–74.0	145–870	605

Explosive substance	Explosive limits in air		Ignition temperature
	in vol.%	in g/m ³	in °C
o-Cresol	1.3	58	555
Methane	5.0–15.0	33–100	(650)
Methanol	5.5–31.0	73–410	455
Methyl acetate	3.1–16.0	95–500	475
Methyl bromide	8.6–20.0	335–790	535
Methyl chloride	7.6–19.0	160–410	625
Methylene chloride	13.0–22.0	450–780	605
Nitrobenzene	1.8	90	480
Phthalic anhydride	1.7–10.5	100–650	580
Propane	2.1–9.5	39–180	470
Isopropyl alcohol	2.0–12.0	50–300	425
Carbon disulphide	1.0–60.0	30–1900	95
Toluene	1.2–7.0	46–270	535
Vinyl chloride	3.8–31.0	95–805	415
Hydrogen	4.0–75.6	3–64	560
o-Xylene	1.0–6.0	44–270	465

Explosive limits and ignition temperatures of selected flammable gases and vapours according to the Nabert-Schön/Römpf Chemie Lexikon, published by Jürgen Falbe, Manfred Reglitz, Georg Thieme Verlag Stuttgart, New York 1995.

Appendix 2: Glossary of terms.

Some of the main terms used in connection with explosion protection have been compiled and defined in the following table. The definitions were largely based on the ATEX equipment directive 94/9/EC.

Auto-ignition temperature	Auto-ignition is a process whereby a substance ignites in the presence of air without an external source of ignition. The process is based on an exothermic oxidation reaction which mainly occurs in solids with a large surface area (e.g. dust), but also in low-volatility organic liquids when distributed on base materials with a large surface area. The auto-ignition temperature is then defined as the temperature at which the rate of heat production exceeds the heat dissipated. The data that has been published can only be used as reference values, however, the temperatures can depend a great deal on other variables (e.g. shape and size of the material or sample and the test method used). The auto-ignition temperature is often referred to as the ignition temperature.
Density ratio	The ratio of a gas or vapour to the density of air.
Evaporation number	Time a liquid takes to evaporate relative to the evaporation time of diethyl ether.
Explosion	An explosion is an exothermic chemical reaction of a flammable substance in gaseous or dispersed solid form with another substance, such as atmospheric oxygen. The explosive velocity will range between 1–1000 m/s and the pressure increase will be in the order of 3–10 bar.
Explosive atmosphere	An explosive atmosphere contains explosive mixtures of gases, vapours, mists or dusts with air, including usual admixtures (e.g. humidity), under atmospheric conditions.
Explosive mixture	An explosive mixture is a mixture of gases or vapours, which may also include mists or dusts, in which a reaction propagates by itself after ignition has occurred.

Explosive limit, lower (LEL) in vol.%

EN 1839

Explosive limit, upper (UEL) in vol.%

EN 1839

Flammable liquids

Flammable gases

Flash point (TFI)

Hazard classes

Hazardous explosive atmosphere

Ignition temperature (T)

EN 14522

Limiting oxygen concentration (LOC)

The lower limit of the concentration of a flammable substance in a mixture with air within which a flame that is independent of the ignition source is no longer able to propagate by itself after ignition.

The upper limit of the concentration of a flammable substance in a mixture with air within which a flame that is independent of the ignition source is no longer able to propagate by itself after ignition. The upper explosive limit is considerably higher in mixtures containing oxygen than in those containing air. Both explosive limits are temperature- and pressure-dependent.

Flammable liquids are substances that have a flash point; at 35 °C they are neither solid nor unctuous and at 50 °C they have a vapour pressure of 3 bar or lower. They are grouped into a number of hazard classes.

Flammable gases are gases that have an explosive range on contact with air at normal pressure.

The flash point of a flammable liquid is the lowest temperature at an air pressure of 760 torr (1013 mbar) at which vapours emerge from the liquid contained in an open or closed cup in such a quantity that a flammable vapour/air mixture forms on application of an external source of ignition.

The German Regulation on Flammable Liquids (VbF) groups flammable liquids into the following hazard classes:

A: Water-insoluble liquids with a flash point under 100 °C

AI: The flash point lies under 21 °C.

AI: The flash point lies between 21 °C and 55 °C.

AI: The flash point lies between 55 °C and 100 °C.

B: Liquids with a flash point lower than 21 °C which are soluble in water at 15 °C in any proportion.

An explosive atmosphere present in hazardous quantities. An atmosphere is considered hazardous when, if ignited, personal injury can be caused as a direct or indirect result of an explosion.

The ignition temperature is the lowest temperature of a hot surface determined in a specified experiment set-up at which the most ignitable flammable gas/air mixture can be caused to combust with a flame at a total pressure of 1.013 bar.

This is the maximum concentration of oxygen in an air/inert gas/gas mixture at which no explosion can occur.

Minimum ignition energy (E_{\min})

The minimum ignition energy of a gas/vapour and air mixture is the smallest amount of electrical energy occurring upon discharge of a capacitor which sufficiently ignites the most ignitable mixture of a gas or vapour with air at atmospheric pressure and a temperature of 20 °C.

Maximum experimental safe gap (MESG)

A standard method is used to determine the maximum experimental safe gap for each gas mixture. The level of ignitability is determined by the gas mixture that emerges from a gap. Gases and vapours are classified into the following explosion groups on the basis of their maximum experimental safe gap:

MESG	Explosion group
> 0.9 mm	II A
0.5 mm ≥ 0.8 mm	II B
< 0.5 mm	II C

Minimum ignition energy (E_{\min})

The minimum ignition energy of a gas/vapour and air mixture is the smallest amount of electrical energy occurring upon discharge of a capacitor which sufficiently ignites the most ignitable mixture of a gas or vapour with air at atmospheric pressure and a temperature of 20 °C.

Temperature class (T1 bis T6)

The temperature classes define ignition ranges into which flammable gases and liquids are classified according to their specific ignition temperature.

IEC 60079-4

Temperature class	Ignition range in °C	Max. surface temp. in °C
T1	> 450	450
T2	> 300 ≤ 450	300
T3	> 200 ≤ 300	200
T4	> 135 ≤ 200	135
T5	> 100 ≤ 135	100
T6	> 85 ≤ 100	85

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