

# **Guide to Gases and Vapours**

## **Properties of dangerous Gases and Vapours**

Flammable and toxic gases and vapours may occur in many places. To deal with the toxic risk and the danger of explosion – this is what gas detection systems are for.

This brochure is meant to give a basic introduction to gas detection technology, measuring principles and the safety concerns.

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## What is Gaseous Matter?

Matter with a temperature above its boiling point is said to be a gas. In respect to the environment of people (normal conditions) any substance having a boiling point below 20 °C at normal pressure is a gas. The most light-weight gas is hydrogen (H<sub>2</sub>, 14-times lighter than air), the heaviest gas is tungsten hexafluoride (WF<sub>6</sub>, approx. ten-times heavier than air).

Under normal conditions 1 cm<sup>3</sup> gas contains about 30·10<sup>18</sup> molecules, the average distance in between is only about three nanometers. They swarm through the space by some 100 to 1000 meters per second, collide some billion times per second with other molecules, so that between two collisions they can only fly approx. 50 to 100 nanometers.

And with each collision they change their flight direction and transfer energy to the collision partner.

This is an entirely random movement of molecules, which macroscopically is measurable as gas temperature (average kinetic energy of all molecules) and gas pressure (average momentum of all molecules striking a surface) or extension (volume). Therefore pressure, temperature and volume mathematically are in a fix relationship, which in the ideal case follow the so called ideal gas law:

- **at constant pressure a gas volume changes proportional to its temperature** – e.g. it expands when being heated
- **at constant gas volume (gas in a closed vessel) the gas pressure changes proportional to its temperature** – e.g. the inner pressure of a closed vessel rises when being heated
- **at constant temperature the gas pressure changes proportional to its volume** – e.g. the pressure rises when the gas is compressed

Also, the extremely quick random movement of gas molecules is the reason that gases mix up easily and never ever will segregate from each other. The movement of molecules into the direction of lower concentration (so-called diffusion) is based on these molecular characteristics and plays an essential role in the measuring principles of gas sensors. Commonly diffusion processes are quicker the faster the molecules move (the hotter the gas is) and the lower the molar weight is (the lighter the gas is).

## Vapours? Why not Gases?

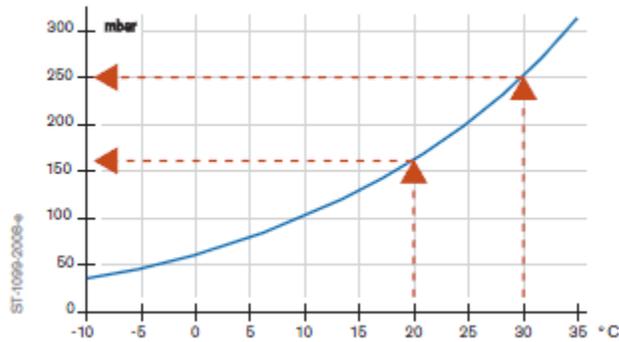
In opposite to gases – there might exist only approx. 200 to 300 – the proper term for the gaseous state of matter below its boiling point is vapour. Vapour mostly exists in an equilibrium with its liquid (or sometimes even solid) phase and condenses or evaporates depending on its temperature.

This behaviour is well-known from water: Cooling down the humid air during nighttime causes fog (condensation), while the warmth of the morning sun dissolves the fog again (evaporation).

In a closed vessel, above the surface of a liquid the maximum possible vapour concentration is always formed. This vapour concentration depends on the liquid's temperature. In a microscopic view, vapour is generated by the random movement of the liquid's molecules and their ability that they can overcome the surface tension and mix-up with the air molecules above.

Each liquid has a certain characteristic vapour pressure which only depends on the liquid's temperature, and this pressure is equal to the atmospheric pressure when its temperature reaches the boiling point. The graph of this correlation is known as the vapour pressure curve, enabling us to determine the maximum possible vapour concentration at a given temperature.

Vapour pressure curve of liquid n-Hexane



Dividing the maximum possible vapour pressure by the ambient pressure results in the so-called saturation concentration in Vol%. E.g., for n-hexane at 20 °C (vapour pressure 162 mbar) at an ambient pressure of 1000 mbar the maximum possible n-hexane concentration is 16.2 Vol%.

## Our Atmosphere

While decreasing its specific weight continuously, our atmosphere is extending far into the deep space. The sky's blue colour is caused by scattering of the sun light at the air's molecules (mainly nitrogen and oxygen), but at a height of about 21 km the sky is black. Compressing the whole atmosphere to constant pressure of roughly 1 bar its height would be 8 km and the UV-absorbing stratospheric ozone layer would be only 3 mm thick.

Typical composition of the earth's atmosphere in ppm:

Gas	Composition	
	dry	humid
<b>Main gases</b>		
N <sub>2</sub> - Nitrogen	780 840	768 543
O <sub>2</sub> - Oxygen	209 450	206 152
H <sub>2</sub> O - Water vapour	0	15 748
Ar - Argon	9 340	9 193
CO <sub>2</sub> - Carbon dioxide	340	335
<b>Trace gases</b>		
Ne - Neon	18	18
He - Helium	5	5
CH <sub>4</sub> - Methane	1.8	1.8
Kr - Krypton	1.1	1.1
H <sub>2</sub> - Hydrogen	0.5	0.5
N <sub>2</sub> O - Nitrous oxide	0.3	0.3
CO - Carbon monoxide	0.09	0.09
Xe - Xenon	0.09	0.09
O <sub>3</sub> - Ozone	0.07	0.07
further trace gases	3.05	3.0
<b>in total</b>	<b>1000 000</b>	<b>1000 000</b>

1 Vol% = 10 000 ppm (= parts per million); assumption: rel. humidity 68 % RH at 20 °C

The mass of the earth's atmosphere is about more than 5 000 trillion tons (5.235·10<sup>18</sup> kg) pressing down on the earth's surface of 500 trillion square meters (0.507·10<sup>15</sup> m<sup>2</sup>). This is the reason why we have an atmospheric pressure of 10 325 kg/m<sup>2</sup>, or, more familiar: 1 013 mbar. With increasing height the atmospheric pressure decreases:

Altitude	Pressure	Altitude	Pressure
-1000 m	1148 mbar	2000 m	795 mbar
- 500 m	1078 mbar	3000 m	701 mbar
0 m	1013 mbar	4000 m	616 mbar
500 m	952 mbar	5000 m	540 mbar
1000 m	900 mbar	6000 m	472 mbar
1500 m	840 mbar	8000 m	356 mbar

Since less molecules are present in a given volume at lower atmospheric pressure, the signal of partial pressure measuring gas detectors is always depending on the atmospheric pressure.

## Oxygen

**While nitrogen, with more than 78 Vol% the main gas of our atmosphere, is completely inert (despite its excess it can not even be used in this gaseous state by plants as a much needed fertilizer), oxygen is very reactive and the base of our breathing and existence, more over: the base of nearly every being.**

There is nearly 21 Vol% oxygen in our atmosphere. Oxygen deficiency is life threatening and cannot be detected by our nose. In general oxygen deficiency is caused by the release of inert gases which displace oxygen. Since roughly one fifth of the atmosphere is oxygen, the oxygen concentration is only reduced by a fifth of the inert gas concentration.

If e.g. 10 Vol% of helium is released into the atmosphere the oxygen concentration decreases by 2 Vol% while the nitrogen concentration is reduced by 8 Vol%.

The industrial use of liquefied nitrogen (- 196 °C) in great amounts may cause dangerous oxygen deficiency due to leaks and sudden nitrogen evaporation.

**Enhanced oxygen concentrations** (e.g. more than 25 Vol%) cannot be sensed by people, but have severe consequences in respect to the flammability characteristics of materials, and may even cause auto-ignition.

This is the reason why explosion protection measures are only related to the atmospheric oxygen concentration.

**When will it be dangerous?**

Oxygen concentration in Vol%	Oxygen partial pressure in mbar	Symptoms
below 17	below 170	Tendency of danger by oxygen deficiency
11 to 14	110 to 140	Unperceived decrease of physical and mental capabilities
8 to 11	80 to 110	Possibility of sudden unconsciousness without warning after a certain time of exposure
6 to 8	60 to 80	Loss of consciousness within a few minutes, resuscitation possible if instantly done
less than 6	less than 60	Sudden loss of consciousness

## **Ex - Ox - Tox ... Danger!**

Virtually, gases and vapours are always dangerous! If gases do not exist in their familiar and respirable atmospheric composition, safe breathing might already be affected.

Moreover: Any gas is potentially dangerous, being liquefied, compressed or in normal state - essential is only their concentration.

### **Basically there are three categories of risk**

- **Ex – Risk of explosion** by flammable gases

- **Ox – Oxygen**

  - Risk of asphyxiation by oxygen displacement

  - Risk of increase of flammability by oxygen enrichment

- **Tox – Risk of poisoning** by toxic gases

Without auxiliary tools humans are not able to recognize these dangers early enough to initiate appropriate counter measures. With only some exceptions our nose has turned out to be an extremely unreliable warning instrument.

For example, hydrogen sulfide in low concentrations is sensible by its typical odor of rotten eggs, but lethal high concentrations of hydrogen sulfide are not detectable by our nose. Escaping into areas assumed to be non-dangerous because of the missing smell has already caused a lot of fatal accidents.

Even harmless gases such as argon, helium or nitrogen may become dangerous when the vitally important oxygen is displaced by a sudden release. Danger of suffocation!

Oxygen concentrations of less than 6 Vol% are known to be lethal. Oxygen in excess (more than 21 Vol%) increases the danger of flammability and might even cause auto-ignition of flammable material. Not only can flammable gases and vapours cause considerable plant damages by ignition, also human life is compromised.

**It is essential to detect Ex-Ox-Tox dangers reliably and to protect human life, assets and environment by means of appropriate measures.**

- This is what gas detectors are required for

- This is what gas detection systems are required for.

## Toxic Gases and Vapours

The toxicity of industrially utilized gases and vapours is determined by means of laboratory experiments resulting in the LC50 rate. From this and from further scientific and occupational health investigations with even lower concentrations authorized committees deduce proposals for threshold limit values (occupational exposure limits) that shall become mandatory.

These threshold limit values are defined so that an employee will not be harmed as long as he is not breathing in higher gas concentrations as the stated threshold limit value during his whole working life – however, this has to be ensured!

The concentrations of these limit values range over seven magnitudes:

limit value	representative substance with this limit value
5000 ppm	Carbon dioxide
1000 ppm	Propane, Butane
500 ppm	Acetone
200 ppm	Methyl ethyl ketone (MEK)
100 ppm	Butanol
50 ppm	n-Hexane, Toluene
20 ppm	Acetonitrile
10 ppm	Chlorobenzene
5 ppm	Diethyl amine
1 ppm	1.1.2.2-Tetrachloroethane
500 ppb	Chlorine
200 ppb	Methyl chloroformate
100 ppb	Chlorine dioxide
50 ppb	Decaborane
20 ppb	Phosgene
10 ppb	Methylisocyanate
5 ppb	MDI (Methyldiphenyldiisocyanate)

**T+ very toxic**       $LC_{50} < 0.5 \text{ g/m}^3$

Boron trichloride, Boron trifluoride, Bromine, Diborane, Fluorine, Hydrogen arsenide, Hydrogen cyanide, Hydrogen fluoride, Hydrogen phosphide, Hydrogen sulfide, Nitrogen dioxide, Nitrogen monoxide, Ozone, Phosgene, Sulfur tetrafluoride, Tungsten hexafluoride

**T Toxic**               $LC_{50} = 0.5 \dots 2.0 \text{ g/m}^3$

Acetonitrile, Ammonia, Benzene, Carbon disulfide, Carbon monoxide, Chlorine, Dicyan, Hydrogen chloride, Methanol, Methyl bromide, Nitrogen trifluoride, Sulfur dioxide

The abbreviation  $LC_{50}$  stands for lethal concentration. Its value reflects the gas concentration in air which will kill 50 % of laboratory animals (mostly mice or rats) when inhaled for a certain time (mostly four hours).

## Flammable Gases and Vapours

**Flammable gases:** The lower their lower explosion limit (LEL), the more dangerous they are.

**Flammable vapours:** The lower their flashpoint, the more dangerous they are. The flashpoint is defined by the liquid's temperature dependent vapour pressure and its LEL.

Vapour	LEL in Vol-%	LEL in g/m <sup>3</sup>	Flash- point in °C	Vapour pressure at 20 °C in mbar	Ignition temperature in °C
Acetone	2.5	60.5	< - 20	246	535
Acrylonitrile	2.8	61.9	-5	117	480
Benzene	1.2	39.1	- 11	100	555
n-Butanol	1.7	52.5	35	7	325
n-Butyl acetate	1.2	58.1	27	11	390
n-Butyl acrylate	1.2	64.1	37	5	275
Chlorobenzene	1.3	61.0	28	12	590
Cyclohexane	1.0	35.1	- 18	104	260
Cyclopentane	1.4	40.9	- 51	346	320
1,2-Dichloroethane (EDC)	6.2	255.7	13	87	440
Diethyl ether	1.7	52.5	-40	586	175
1,4-Dioxane	1.9	69.7	11	38	375
Epichlorohydrin	2.3	88.6	28	16	385
Ethanol	3.1	59.5	12	58	400
Ethyl acetate	2.0	73.4	- 4	98	470
Ethyl benzene	1.0	44.3	23	10	430
n-Hexane	1.0	35.9	- 22	160	240
Methanol	6.0	80.0	9	129	440
1-Methoxy-2-propanol	1.8	67.6	32	12	270
Methylethyl ketone (MEK)	1.5	45.1	- 10	105	475
Methyl methacrylate	1.7	70.9	10	40	430
n-Nonane	0.7	37.4	31	5	205
n-Octane	0.8	38.1	12	14	205
n-Pentane	1.4	42.1	- 40	562	260
i-Propanol (IPA)	2.0	50.1	12	43	425
Propylene oxide	1.9	46.0	- 37	588	430
Styrene	1.0	43.4	32	7	490
Tetrahydrofurane (THF)	1.5	45.1	- 20	200	230
Toluene	1.1	42.2	6	29	535
Xylene (mix of isomers)	1.0	44.3	25	7	465

Gas	LEL in Vol-%	LEL in g/m <sup>3</sup>	Ignition temperatur in °C
Acetylene	2.3	24.9	305
Ammonia	15.4	109.1	630
1,3-Butadiene	1.4	31.6	415
i-Butane	1.5	36.3	460
n-Butane	1.4	33.9	365
n-Butene (Butylene)	1.2	28.1	360
Dimethyl ether	2.7	51.9	240
Ethene (Ethylene)	2.4	28.1	440
Ethylene oxide	2.6	47.8	435
Hydrogen	4.0	3.3	560
Methane	4.4	29.3	595
Methyl chloride	7.6	159.9	625
Propane	1.7	31.2	470
Propene (Propylene)	1.8	31.6	485

Only flammable liquids have a flashpoint.

By definition there is no flashpoint for gases.

## LEL and Preventive Explosion Protection

**Only if the proportion of a fuel in air is within certain limits flammable gases and vapours can produce flammable mixtures with air.**

The lower explosion limit (LEL) is defined as the concentration (given in Vol%) of a fuel gas/air-mixture which under standardized conditions can be ignited and continues to burn.

The LEL of all known flammable gases and vapours is in the range of approx. 0.5 through 15 Vol%.

For example, the LEL of hydrogen-air- mixtures is 4 Vol%, and so a test gas of 2 Vol% in air is definitely not ignitable.

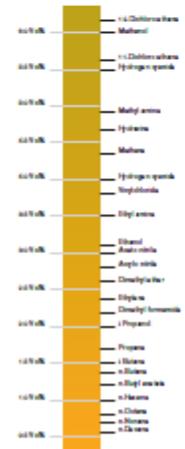
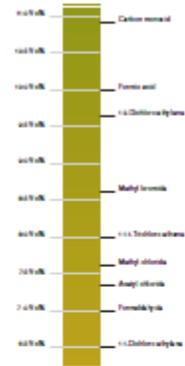
### Concentration limitation

This behaviour is very essential for the practice of explosion protection:

As a flammable gas below its LEL concentration cannot be ignited, explosion protection can be performed by continuously measuring the gas concentration and making sure by appropriate measures that e.g. half of the LEL (= 50% LEL) is never exceeded.

This method of preventive explosion protection is known to be the primary measure: Not the ignition of a potentially explosive atmosphere, but the forming of a potentially explosive atmosphere is reliably prevented.

Concentration measurement is preferably performed by means of infrared sensors or catalytic bead sensors, which must comply with special standardized safety requirements and being certified for this purpose.



## Flashpoint of Flammable Liquids

Although speaking of flammable liquids, it is not the liquid state but the vapour being flammable. Only vapour can form a flammable mixture with the air's oxygen.

Both the volatility of the vapour and its lower explosion limit (LEL) are a measure for the risk of explosion. The properties volatility and LEL are combined by the so-called flashpoint.

To be ignitable at all, the concentration of the liquid's vapour above the liquid's surface needs to exceed the LEL. If it does or doesn't depends on the individual vapour concentration produced by the liquid's vapour pressure – and this is depending on the liquid's temperature only.

In respect to the safety of flammable goods this behaviour is described by the flashpoint (F):

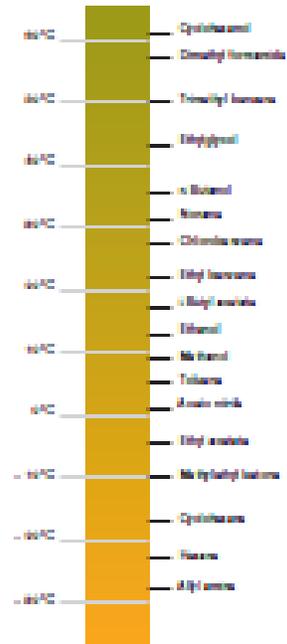
The flashpoint is the temperature at which just so much vapour is produced that the vapour-air mixture can be ignited by a standardized apparatus and continues to burn. For example, if the flashpoint of a flammable liquid is above 50 °C, this liquid cannot be ignited at 30 °C.

Conclusion: flammable liquids are the more dangerous the lower their flashpoint.

Since vapours of flammable liquids cannot be ignited below their flashpoint, this may be the basis of preventive explosion protection: Only use flammable liquids with flashpoints higher than the ambient temperature and there is no risk of explosion.

Indeed this is common practice, but if the liquids are used as solvents there is a disadvantage: Less volatile liquids require more energy for evaporation.

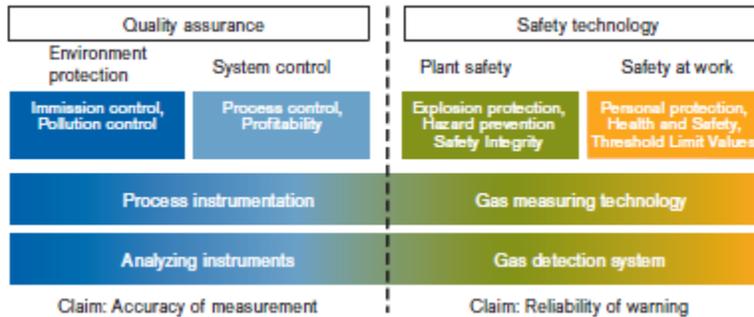
By definition, gases do not have a flashpoint because they have no liquid phase under normal conditions.



You cannot ignite Diesel (F > 55 °C) by means of a burning match, but you can ignite gasoline (F < - 20 °C)

## Gas Detection Systems

In a first approach gas detection instruments are products of safety technology and are used preferably to protect workers and to ensure plant safety. Gas detection systems are dedicated to detect dangerous gas concentrations, to trigger alarms and – as far as possible – to activate counter measures, before it can come to a hazardous situation for employees, assets and environment.



Gas detection instruments may be portable (or semi-portable) gas measuring instruments or fixed installed gas detection systems. The safety of an area potentially being affected by dangerous gases and vapours to a high degree depends on the reliability of the gas detection system, and especially on the quality of the sensors being used. In opposite to sensors of portable devices fixed installed sensors including their electronics are continuously in operation year for year for 24 hours a day – just to be available for the instance of a random gas release. And this even under extreme environmental conditions, at e.g. - 50 °C or + 65 °C, at high relative humidity or even very dry atmospheres, in outdoor applications with rain, storm and snow or hot desert conditions, electromagnetic disturbances or strong vibration ... And – self evident – explosion protection must not be an issue and measuring performance shall only be affected insignificantly. As shown in the graphics, there is a fluent crossover between gas detection technology on the one side and process instrumentation on the other side. Although developed as a product of safety technology, there are certain gas detection transmitters having so excellent measuring performance characteristics that today they even show up more and more as analyzing instruments in the field of process instrumentation.