Introduction to Gas Detection Systems
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 (H₂, 14-times lighter than air), the heaviest gas is tungsten hexafluoride (WF₆, approx. ten-times heavier than air).

Under normal conditions 1 cm³ gas contains about 30·10¹⁸ 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 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).
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.

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%.
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:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dry</td>
</tr>
<tr>
<td><strong>Main gases</strong></td>
<td></td>
</tr>
<tr>
<td>N₂ - Nitrogen</td>
<td>780</td>
</tr>
<tr>
<td>O₂ - Oxygen</td>
<td>209</td>
</tr>
<tr>
<td>H₂O - Water vapour</td>
<td>0</td>
</tr>
<tr>
<td>Ar - Argon</td>
<td>9 340</td>
</tr>
<tr>
<td>CO₂ - Carbon dioxide</td>
<td>340</td>
</tr>
<tr>
<td><strong>Trace gases</strong></td>
<td></td>
</tr>
<tr>
<td>Ne - Neon</td>
<td>18</td>
</tr>
<tr>
<td>He - Helium</td>
<td>5</td>
</tr>
<tr>
<td>CH₄ - Methane</td>
<td>1.8</td>
</tr>
<tr>
<td>Kr - Krypton</td>
<td>1.1</td>
</tr>
<tr>
<td>H₂ - Hydrogen</td>
<td>0.5</td>
</tr>
<tr>
<td>N₂O - Nitrous oxide</td>
<td>0.3</td>
</tr>
<tr>
<td>CO - Carbon monoxide</td>
<td>0.09</td>
</tr>
<tr>
<td>Xe - Xenon</td>
<td>0.09</td>
</tr>
<tr>
<td>O₃ - Ozone</td>
<td>0.07</td>
</tr>
<tr>
<td>further trace gases</td>
<td>3.05</td>
</tr>
<tr>
<td>in total</td>
<td>1000 000</td>
</tr>
</tbody>
</table>

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 (5.235·10¹⁸ kg) pressing down on the earth’s surface of 500 trillion square meters (0.507·10¹⁵ m²). This is the reason why we have an atmospheric pressure of 10 325 kg/m², or, more familiar: 1 013 mbar. With increasing height the atmospheric pressure decreases:

<table>
<thead>
<tr>
<th>Altitude</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1000 m</td>
<td>1148 mbar</td>
</tr>
<tr>
<td>- 500 m</td>
<td>1078 mbar</td>
</tr>
<tr>
<td>0 m</td>
<td>1013 mbar</td>
</tr>
<tr>
<td>500 m</td>
<td>952 mbar</td>
</tr>
<tr>
<td>1000 m</td>
<td>900 mbar</td>
</tr>
<tr>
<td>1500 m</td>
<td>840 mbar</td>
</tr>
<tr>
<td>2000 m</td>
<td>796 mbar</td>
</tr>
<tr>
<td>3000 m</td>
<td>701 mbar</td>
</tr>
<tr>
<td>4000 m</td>
<td>616 mbar</td>
</tr>
<tr>
<td>5000 m</td>
<td>540 mbar</td>
</tr>
<tr>
<td>6000 m</td>
<td>472 mbar</td>
</tr>
<tr>
<td>8000 m</td>
<td>356 mbar</td>
</tr>
</tbody>
</table>

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.
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?

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


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.
The toxicity of industrially utilized gases and vapours is determined by means of laboratory experiments resulting in the $\text{LC}_{50}$ 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:

<table>
<thead>
<tr>
<th>limit value</th>
<th>representative substance with this limit value</th>
</tr>
</thead>
<tbody>
<tr>
<td>5000 ppm</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>1000 ppm</td>
<td>Propane, Butane</td>
</tr>
<tr>
<td>500 ppm</td>
<td>Acetone</td>
</tr>
<tr>
<td>200 ppm</td>
<td>Methyl ethyl ketone (MEK)</td>
</tr>
<tr>
<td>100 ppm</td>
<td>Butanol</td>
</tr>
<tr>
<td>50 ppm</td>
<td>n-Hexane, Toluene</td>
</tr>
<tr>
<td>20 ppm</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>10 ppm</td>
<td>Chlorobenzene</td>
</tr>
<tr>
<td>5 ppm</td>
<td>Dethyl amine</td>
</tr>
<tr>
<td>1 ppm</td>
<td>1.1.2.2-Tetrachloroethane</td>
</tr>
<tr>
<td>500 ppb</td>
<td>Chlorine</td>
</tr>
<tr>
<td>200 ppb</td>
<td>Methyl chloroformate</td>
</tr>
<tr>
<td>100 ppb</td>
<td>Chlorine dioxide</td>
</tr>
<tr>
<td>50 ppb</td>
<td>Decaborane</td>
</tr>
<tr>
<td>20 ppb</td>
<td>Phosgene</td>
</tr>
<tr>
<td>10 ppb</td>
<td>Methylisocyanate</td>
</tr>
<tr>
<td>5 ppb</td>
<td>MDI (Methylidiphenyliisocyanate)</td>
</tr>
</tbody>
</table>

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


$T$ Toxic $\text{LC}_{50} = 0.5 \ldots 2.0 \text{ g/m}^3$

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

The abbreviation $\text{LC}_{50}$ 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: 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.

<table>
<thead>
<tr>
<th>Vapour</th>
<th>LEL in Vol-%</th>
<th>LEL in g/m³</th>
<th>Flashpoint in °C</th>
<th>Vapour pressure at 20 °C in mbar</th>
<th>Ignition temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>2.5</td>
<td>60.5</td>
<td>-20</td>
<td>246</td>
<td>535</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>2.8</td>
<td>61.9</td>
<td>-5</td>
<td>117</td>
<td>480</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.2</td>
<td>39.1</td>
<td>-11</td>
<td>100</td>
<td>555</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>1.7</td>
<td>52.5</td>
<td>35</td>
<td>7</td>
<td>325</td>
</tr>
<tr>
<td>n-Butyl acetate</td>
<td>1.2</td>
<td>58.1</td>
<td>27</td>
<td>11</td>
<td>390</td>
</tr>
<tr>
<td>n-Butyl acrylate</td>
<td>1.2</td>
<td>64.1</td>
<td>37</td>
<td>5</td>
<td>275</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>1.3</td>
<td>61.0</td>
<td>28</td>
<td>12</td>
<td>590</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.0</td>
<td>35.1</td>
<td>-18</td>
<td>104</td>
<td>260</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>1.4</td>
<td>40.9</td>
<td>-51</td>
<td>346</td>
<td>320</td>
</tr>
<tr>
<td>1,2-Dichloroethane (EDC)</td>
<td>6.2</td>
<td>255.7</td>
<td>13</td>
<td>87</td>
<td>440</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>1.7</td>
<td>52.5</td>
<td>-40</td>
<td>586</td>
<td>175</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>1.9</td>
<td>69.7</td>
<td>11</td>
<td>38</td>
<td>375</td>
</tr>
<tr>
<td>Epichlorohydrin</td>
<td>2.3</td>
<td>88.6</td>
<td>28</td>
<td>16</td>
<td>385</td>
</tr>
<tr>
<td>Ethanol</td>
<td>3.1</td>
<td>59.5</td>
<td>12</td>
<td>58</td>
<td>400</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>2.0</td>
<td>73.4</td>
<td>-4</td>
<td>98</td>
<td>470</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>1.0</td>
<td>44.3</td>
<td>23</td>
<td>160</td>
<td>430</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>1.0</td>
<td>35.9</td>
<td>-22</td>
<td>160</td>
<td>240</td>
</tr>
<tr>
<td>Methanol</td>
<td>6.0</td>
<td>80.0</td>
<td>9</td>
<td>129</td>
<td>440</td>
</tr>
<tr>
<td>1-Methoxy-2-propanol</td>
<td>1.8</td>
<td>67.6</td>
<td>32</td>
<td>12</td>
<td>270</td>
</tr>
<tr>
<td>Methyl methacrylate</td>
<td>1.7</td>
<td>70.9</td>
<td>10</td>
<td>40</td>
<td>430</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>0.7</td>
<td>37.4</td>
<td>31</td>
<td>5</td>
<td>205</td>
</tr>
<tr>
<td>n-Octane</td>
<td>0.8</td>
<td>38.1</td>
<td>12</td>
<td>14</td>
<td>205</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>1.4</td>
<td>42.1</td>
<td>-40</td>
<td>562</td>
<td>260</td>
</tr>
<tr>
<td>n-Propanol (IPA)</td>
<td>2.0</td>
<td>50.1</td>
<td>12</td>
<td>43</td>
<td>425</td>
</tr>
<tr>
<td>Propylene oxide</td>
<td>1.9</td>
<td>46.0</td>
<td>-37</td>
<td>588</td>
<td>430</td>
</tr>
<tr>
<td>Styrene</td>
<td>1.0</td>
<td>43.4</td>
<td>32</td>
<td>7</td>
<td>490</td>
</tr>
<tr>
<td>Tetrahydrofuran (THF)</td>
<td>1.5</td>
<td>45.1</td>
<td>-20</td>
<td>200</td>
<td>230</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.1</td>
<td>42.2</td>
<td>6</td>
<td>29</td>
<td>535</td>
</tr>
<tr>
<td>Xylene (mix of isomers)</td>
<td>1.0</td>
<td>44.3</td>
<td>25</td>
<td>7</td>
<td>465</td>
</tr>
</tbody>
</table>

Gas LEL in Vol-% LEL in g/m³ Ignition temperature in °C

<table>
<thead>
<tr>
<th>Gas</th>
<th>LEL in Vol-%</th>
<th>LEL in g/m³</th>
<th>Ignition temperature in °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>2.3</td>
<td>24.9</td>
<td>305</td>
</tr>
<tr>
<td>Ammonia</td>
<td>15.4</td>
<td>109.1</td>
<td>630</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>1.4</td>
<td>31.6</td>
<td>415</td>
</tr>
<tr>
<td>i-Butane</td>
<td>1.5</td>
<td>36.3</td>
<td>460</td>
</tr>
<tr>
<td>n-Butane</td>
<td>1.4</td>
<td>33.9</td>
<td>365</td>
</tr>
<tr>
<td>n-Butene (Butylene)</td>
<td>1.2</td>
<td>28.1</td>
<td>360</td>
</tr>
<tr>
<td>Dimethyl ether</td>
<td>2.7</td>
<td>51.9</td>
<td>240</td>
</tr>
<tr>
<td>Ethene (Ethylene)</td>
<td>2.4</td>
<td>28.1</td>
<td>440</td>
</tr>
<tr>
<td>Ethylene oxide</td>
<td>2.6</td>
<td>47.8</td>
<td>435</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>4.0</td>
<td>3.3</td>
<td>560</td>
</tr>
<tr>
<td>Methane</td>
<td>4.4</td>
<td>29.3</td>
<td>595</td>
</tr>
<tr>
<td>Methyl chloride</td>
<td>7.6</td>
<td>159.9</td>
<td>625</td>
</tr>
<tr>
<td>Propane</td>
<td>1.7</td>
<td>31.2</td>
<td>470</td>
</tr>
<tr>
<td>Propene (Propylene)</td>
<td>1.8</td>
<td>31.6</td>
<td>485</td>
</tr>
</tbody>
</table>

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.
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.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Flashpoint</th>
<th>Flammable Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>Cyclohexanol</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>Dimethyl formamide</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>Trimethyl benzene</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Ethylglycol</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>n-Butanol</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>Nonane</td>
<td></td>
</tr>
<tr>
<td>-10</td>
<td>Chlorobenzene</td>
<td></td>
</tr>
<tr>
<td>-20</td>
<td>Ethyl benzene</td>
<td></td>
</tr>
<tr>
<td>-30</td>
<td>i-Butyl acetate</td>
<td></td>
</tr>
<tr>
<td>-40</td>
<td>Ethanol</td>
<td></td>
</tr>
<tr>
<td>-50</td>
<td>Methanol</td>
<td></td>
</tr>
<tr>
<td>-60</td>
<td>Toluene</td>
<td></td>
</tr>
<tr>
<td>-70</td>
<td>Aceto nitrile</td>
<td></td>
</tr>
<tr>
<td>-80</td>
<td>Ethyl acetate</td>
<td></td>
</tr>
<tr>
<td>-90</td>
<td>Methyl ethyl ketone</td>
<td></td>
</tr>
<tr>
<td>-100</td>
<td>Cyclohexane</td>
<td></td>
</tr>
<tr>
<td>-110</td>
<td>Hexane</td>
<td></td>
</tr>
<tr>
<td>-120</td>
<td>Allyl amine</td>
<td></td>
</tr>
</tbody>
</table>

You cannot ignite Diesel (F > 55 °C) by means of a burning match, but you can ignite gasoline (F < -20 °C)!
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.
Many toxic gases are also very reactive and under suitable conditions they change by chemical reactions. The electrochemical sensor is such a micro-reactor, which at the presence of reactive gases produces electrons just like a battery. The flow of electrons is a very low but measurable electric current.

An electrochemical sensor consists of at least two electrodes (measuring electrode and counter electrode) which have electrical contact in two different ways: On the one hand via an electrical conductive medium called electrolyte (a pasty-like liquid to transport ions), on the other hand via an outer electric current circuit (a simple copper wire to transport electrons):

The electrodes are made of a special material which also has catalytic characteristics enabling certain chemical reactions to take place in the so-called 3-phase zone, where gas, solid catalyst and liquid electrolyte are present. The electron grabber oxygen being needed for this reaction comes from the ambient air. Further electron grabbers are known, e.g. chlorine, fluorine, ozone or nitrogen dioxide. Thus the sensor current of sensors being used for these gases flows in reverse direction. The current can be measured by means of a micro-amp meter.
More than a hundred of gases and vapours are detectable by electrochemical Dräger sensors. Some of these react very specifically to the target gas, others are typical gas group sensors being sensitive to a lot of different reactive gases.

Electrochemical Dräger sensors are mostly equipped with three electrodes, a measuring-, a counter-, and a reference-electrode. The sensor’s measuring performance is increased by means of a bias voltage being measured and kept constant by means of the reference-electrode and an electronic control circuit (so-called potentiostat circuit). Additionally there is a temperature measuring element in the interior of the sensor because electrochemical processes are extremely temperature dependent and need to be compensated accordingly. Only by the outer electrical circuit of the sensor (especially for temperature compensation and amplification and conditioning of the very low and noisy sensor current - only a few micro amperes) which produces a 4-20-mA-signal, the electrochemical sensor turns into a real gas detector. The following measuring ranges can be realized (user adjustable with e.g. Polytron 7000):

<table>
<thead>
<tr>
<th>Gas</th>
<th>minimum full scale deflection</th>
<th>maximum full scale deflection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic Compounds</td>
<td>3 ppm</td>
<td>30 ppm</td>
</tr>
<tr>
<td>Ammonia</td>
<td>50 / 300 ppm</td>
<td>200 / 1000 ppm</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>50 / 200 ppm</td>
<td>1000 / 5000 ppm</td>
</tr>
<tr>
<td>Chlorine</td>
<td>1 ppm</td>
<td>50 ppm</td>
</tr>
<tr>
<td>Hydrazine</td>
<td>0.3 ppm</td>
<td>3 ppm</td>
</tr>
<tr>
<td>Hydrides</td>
<td>0.3 ppm</td>
<td>1 / 20 ppm</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>500 ppm</td>
<td>3000 ppm</td>
</tr>
<tr>
<td>Hydrogen chloride</td>
<td>20 ppm</td>
<td>100 ppm</td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>10 ppm</td>
<td>50 ppm</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>1 / 1000 ppm</td>
<td>50 / 7000 ppm</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>10 / 100 ppm</td>
<td>100 / 1000 ppm</td>
</tr>
<tr>
<td>Nitrogen dioxide</td>
<td>5 ppm</td>
<td>100 ppm</td>
</tr>
<tr>
<td>Nitrogen monoxide</td>
<td>30 ppm</td>
<td>200 / 500 ppm</td>
</tr>
<tr>
<td>Organic Vapours</td>
<td>20 ppm</td>
<td>100 / 200 ppm</td>
</tr>
<tr>
<td>Ozone</td>
<td>0.5 ppm</td>
<td>5 ppm</td>
</tr>
<tr>
<td>Oxygen</td>
<td>5 Vol%</td>
<td>25 / 100 Vol%</td>
</tr>
<tr>
<td>Phosgene</td>
<td>0.1 ppm</td>
<td>1 ppm</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>5 ppm</td>
<td>100 ppm</td>
</tr>
</tbody>
</table>

The electrochemical sensor needs very low electric power and can thus be operated intrinsically safe. In this case problems with heavy flameproof enclosures do not apply and sensor replacement at site can be carried out very easily and without hot work permit.
Under certain circumstances flammable gases and vapours can be oxidized by means of the air’s oxygen to release heat of reaction. Typically this is achieved by special and suitable heated catalyst material, which slightly increases its temperature by the heat of reaction. This increase of temperature is a measure for the gas concentration.

So-called pellistors are tiny and very porous ceramic beads (diameter approx. 1 mm) embedding a small platinum wire coil. There is an electric current flowing through the platinum wire coil so that the pellistor is heated up to some hundred degrees Celsius.

If the ceramic bead contains some suitable catalytic material, the pellistor’s temperature will rise in the presence of flammable gas, and the platinum wire coil’s resistance will increase accordingly. This change in resistance in respect to the resistance in clean air is used for electronic evaluation.

To eliminate influences of changes of the ambient temperature, a second pellistor is used, which is very similar but does not respond to gas, because the pellistor does not contain catalyst material or is inhibited otherwise. Integrating both the pellistors in a Wheatstone bridge circuit results in a sensor for concentration measurement of flammable gases, to a large extent independent of the ambient temperature.

\[
\text{CH}_4 + 2 \text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{CO}_2 + \text{heat of reaction}
\]
One pellistor alone is not suitable for the detection of flammable gases and vapours. It needs a second one to compensate for environmental parameters (especially temperature and humidity). And it needs to be explosion protected. By means of a flameproof enclosure and a sinter disk a useful catalytic bead sensor results.

The compensator pellistor is built very similar to the active pellistor, but does not contain catalyst material so that gas cannot be oxidized. If the ambient temperature changes, the resistance of both the pellistors will change and there is no bridge signal. However, if gas is present, only the resistance of the active pellistor changes and the Wheatstone bridge is unbalanced. Since the pellistors of the catalytic bead sensor are heated to about 450 °C, it can act as an ignition source if the LEL is exceeded and the ignition temperature of the gas is lower than 450 °C. By means of a sinter disk the following is prevented: If in the interior of the catalytic bead sensor an ignition takes place, the sensor’s housing will withstand the explosion pressure and the flame is cooled down below the ignition temperature of the gas, and no flame penetrates to the outside. These are the characteristics of the so-called flameproof encapsulation.

Catalytic bead sensors are operated with an electronic circuit called Wheatstone bridge, which is suitable to convert very small resistance changes into a measurable voltage.

If the second half of the Wheatstone bridge is placed in the controller, the catalytic bead sensor may be connected to controllers by means of very long cables. However, they are short when the sensor is installed in a transmitter.
When considering the broad range of flammable gases and vapours one will realize that most of these substances are chemical compounds primarily consisting of carbon, hydrogen, oxygen, and sometimes nitrogen. These so-called organic compounds are called hydrocarbons. Hydrocarbons have special properties which can be used for infrared-measurement of their concentration.

All the gases absorb radiation in a characteristic manner, some even in the visible range (0.4 to 0.8 micrometers). This is why chlorine is green-yellow, bromine and nitrogen dioxide are brown-red, iodine is violet, and so on. However, these colours can only be seen at rather high and lethal concentrations. Hydrocarbons absorb radiation of a certain wavelength range, approx. at 3.3 to 3.5 micrometers, and, since oxygen, nitrogen and argon do not absorb, this can be used for concentration measurement of hydrocarbons in air.

An optical system containing a mixture of e.g. methane or propane in air will attenuate an incoming infrared intensity in a predictable way, and for a given gas this attenuation is depending on only its concentration.

Air: Infrared passes without being attenuated, no reduced intensity, no measuring signal
Gas: Infrared passes by being attenuated, reduced intensity, measuring signal corresponds to the current gas concentration.

This photometer principle is the basis of an infrared measuring instrument. The correlation of measured intensity reduction on the one hand and the gas concentration in the optical system on the other hand, is made by the calibration process: A defined gas concentration will always produce the same intensity reduction and thus always the same measuring signal.

Most of the flammable gases and vapours are hydrocarbons which are almost always detectable by their characteristic infrared absorption.
The measuring principle is simple: Hydrocarbons absorb infrared radiation (IR) in the wavelength range of 3.3 to 3.5 micrometers (μm), more or less, depending on the absorption spectrum of the considered gas. However, the attenuation of the infrared radiation is very small and a challenge concerning the measuring technique. And, unfortunately, the reduction of intensity can also occur by other circumstances, e.g. by contaminated optics or reduction of the infrared radiation source's intensity.

The radiation source of an infrared sensor is a flashing filament lamp, operated with low-voltage, having a high percentage of infrared. Passing an IR-transparent window this radiation is split into two parts by means of a beam splitter, one part for the measuring detector, one part for the reference detector. A detector consists of an encapsulated pyro-electric crystal converting the received radiation energy into a measurable voltage. However, the detectors are different because of their optical interference filters: The crystal of the measuring detector only receives radiation of e.g. 3.4 μm, and the reference detector of e.g. 4.0 μm wavelength. Gases generally do not absorb at 4.0 μm. So, if both the detectors detect a reduced radiation energy, gases surely are not the cause! By means of the reference detector it is possible to make the measurement to a certain degree unsusceptible to contamination of the optics and even to automatically request for preventive maintenance.

IR-Transmitters are equipped with IR sensors like this. The measuring signal of both the detectors is conditioned accordingly and is finally available as a 4 to 20-mA signal at the transmitter’s output. Because of their long lifetime IR-transmitters are favoured in the industrial measurement. In opposite to the electrochemical and catalytic bead sensors the detectors of IR-sensors do not come into contact with the gases to be measured. As long as there is no condensation - and this is inhibited by heated surfaces – IR transmitters perform so excellently that they can be found more and more even in process industry applications.
The high velocity of the gas molecules is the cause that gases expand quickly and also quickly mix up with other gases and never separate again.

And as long as there are concentration differences in the whole mixture the process of mixing is incomplete and does not come to an end.

These concentration differences can also act as a micro pump. If the concentration difference is kept constant there will be a continuous flow of molecules into the direction of the lower concentration — and this effect is used for sensors in gas detection technology, the so-called diffusion-controlled sensors.

The trick: With the catalytic bead sensor and the electrochemical sensor the target gas is consumed by chemical reaction, directly on the place of reaction we have a gas concentration of nearly zero, far less then in the ambient area, producing a depletion zone. So there is a forced concentration difference and gas molecules are flowing into the sensor’s reaction area.

Illustration: Because of the molecular movement the nature does not keep calm until the three bigger molecules are homogeneously dispersed over the entire gas volume. After uniform distribution the diffusion process ends.

Convection to the sensor, diffusion into the sensor

While gas essentially gets to the sensor by means of natural convection, the penetration into the sensor’s interior via sinter disk or dust filter is rather a diffusion controlled process, because pores contain calm air where no convection takes place. Not the pore walls but the calm air is inhibiting the penetration: If a gas molecule would be as big as a pea, a sinter pore or filter pore would have a diameter of some 100 to 1000 meters!

Diffusion controlled sensors do not need a pump.
If you think of an infrared-sensor with an optical path extended for multiple times, this would be a gas detection system with an open path: gas molecules entering this path will cause a measurable IR-absorption. Gas detection systems like this are something like a light barrier for gas molecules. And not only for a few meters, this is true for open path lengths of up to 200 meters!

The measuring result (reading) of an open path measurement is a little bit unusual. While the optical system of an infrared-sensor can be assumed to be homogeneously filled with a defined gas concentration, this is never the case with a long measuring path. Basically one cannot differentiate whether there is a high gas concentration along a small part of the open path or half the concentration along twice the path length: In both cases the measuring signal is the same because each absorbing molecule in the path contributes to the measuring signal, independent from their distribution.

However, in special applications the probability that the gas cloud is drifting through the open path is higher than being detected by a point detector.

In the terms of safety: One abandons the usual concentration measurement for the sake of higher detection probability.

Illustration: As long as the gas cloud stays in the open path there is a measuring signal, independent of the dilution with air. We may say an open path detector is a molecule counter independent of their distances.

So, an open path detector is rather a reliable gas hazard indicator than a concentration measuring instrument. In applications handling a high risk of gas release (e.g. natural gas exploration) the information „gas is present“ is considered to be sufficient to activate safety relevant counter measures.
A stand-alone sensor is not sufficient for gas detection. Sensor signals need to be electronically conditioned (some of them temperature-compensated), locally displayed (for calibration purposes), measuring ranges to be configured – and for all this power is necessary.

It has become worldwide accepted that gas detection transmitters are operated by 24 V DC, and this voltage may vary within wide limits, e.g. between 16 and 30 volts. The transmitter’s electronics convert the sensor signal into an output current so with clean air (zero point) at the sensor a current of 4 mA flows to the control unit, while it is 20 mA at full scale deflection.

If the cable between transmitter and controller is cut, no current will flow (the current is 0 mA), and the controller will recognize this condition, activating a fault alarm. Moreover, signals lower than 3.8 mA or higher than 20.5 mA are not interpreted as a measuring signal but as special signals to indicate underrange (negative measuring values) or overrange, and also special maintenance signals. The 4 to 20 mA-signal is a worldwide accepted industry standard which, in opposite to voltage signals, does not depend on the cable resistance, which has low impedance (resistance) and is relatively immune to electromagnetic interferences.

Transmitters with electrochemical sensors have such a low power consumption that they can be operated with even less than 4 mA, and can draw, depending on the gas concentration, an additional current of 4 to 20 mA from the power supply: Only two wires are needed for power supply and measuring signal. However, transmitters with catalytic bead sensors or infrared-sensors have higher power consumption and require 3 wires for power supply and signal.

The 4 to 20 mA signal can also be used to superpose a symmetrical frequency modulated signal of ± 0.5 mA to exchange additional digital information between controller and transmitter. This is the so-called HART signal, which can also be used to address certain transmitters by their digital addresses and poll their actual measuring signals and more. Several HART-compatible transmitters can communicate on only one 2-core communication cable.

Digital communication, via HART or via the so-called RS 485 interface, enables the customer to remotely query the transmitters’ “well-being” and preventively perform maintenance actions based on the results.
There are many reasons not to have the sensor directly at the location where the target gas (gas to be measured) may occur. Instead of this continuous sampling can be performed which may also have advantages: The gas sample can be pre-conditioned (e.g. by filters), can be dried and tempered, condensate can be trapped, pressure changes can be compensated, and by means of solenoid valves further sampling paths can be activated. Especially test gas can be applied automatically to the sensor.

**Zone spreading**

When sampling from a hazardous area (mostly zone 1) the ex-zone is spread via the sampling tube into the safe area. Since in the safe area there are no means of explosion protection, ignition becomes possible. This can be avoided by using flame arrestors in the sampling tube. Flame arrestors do not inhibit the ignition, but prevent a flash-back into the hazardous area.

**Sampling tubes**

The smaller the sampling tube’s cross section, the higher the pressure drop – the greater the tube’s cross-section, the longer the response time: 4 mm inner diameter and a flow of about 1 to 2 liter per minute is a good compromise.

**Pre-sampling**

Using a strong pump (10 to 20 L/min) gas sampling can be realized over longer distances (up to 100 to 150 m). A second small pump (approx. 1 L/min) should be used to supply the gas sample taken from the pre-sampling tube to the sensor.

**Sampling line monitoring**

Considering the safety relevance it is essential to know that sampling basically increases the response time and that the complete sampling line needs to be monitored for proper function. This is mostly done by a flow meter with switch contacts which, in case of a blocked sampling tube or pump failure, trigger an alarm. If filters or condensate traps are used, they need to be maintained regularly.

**Material and wall adsorption effects**

The tubing material should preferably be PTFE (Teflon), Viton, or stainless steel. Some gases tend to increased adsorption on the material’s surfaces and this may influence the measuring signal especially for ppm-measurement.
Explosion Protection

In industrial processes very frequently flammable substances and sometimes also flammable dusts are involved. In these areas flammable gases and vapours may be released process-related (e.g. by relief valves) but also by unpredictable and hazardous incidents. Preventively these hazardous areas are declared to Ex-areas (“zones”), in which solely equipment may be installed which is equipped with a suitable type of explosion protection and certified accordingly.

Explosion protection is worldwide regulated. The basis of these standards according to IEC, CENELEC (Europe) and NEC 505 (North America) is very similar and is established on the “3-zones-concept”, which is also more and more accepted in the USA,

<table>
<thead>
<tr>
<th>Zone according to IEC, NEC 505 and CENELEC</th>
<th>Dangerous explosive atmospheres are present ...</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 0</td>
<td>continuously, long periods or frequently</td>
</tr>
<tr>
<td>Zone 1</td>
<td>occasionally, likely to occur</td>
</tr>
<tr>
<td>Zone 2</td>
<td>infrequently and for a short period only</td>
</tr>
</tbody>
</table>

while the well-known American way of explosion protection acc. to NEC 500 is based on the “2-divisions-concept”:

<table>
<thead>
<tr>
<th>Division acc. to NEC 500</th>
<th>Dangerous explosive atmospheres are ...</th>
</tr>
</thead>
<tbody>
<tr>
<td>Division 1</td>
<td>likely to exist</td>
</tr>
<tr>
<td>Division 2</td>
<td>not likely to exist</td>
</tr>
</tbody>
</table>

According to IEC, NEC 505 and CENELEC there are seven standardized types of protection for electrical equipment in zone 1, while in North America (USA/Canada) there are only three types of explosion protection for division 1 according to NEC 500:

<table>
<thead>
<tr>
<th>Type of protection acc. to IEC, NEC 505 and CENELEC</th>
<th>comparable type of protection acc. to NEC 500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flameproof enclosure</td>
<td>Explosion proof</td>
</tr>
<tr>
<td>Encapsulation</td>
<td>–</td>
</tr>
<tr>
<td>Powder filling</td>
<td>–</td>
</tr>
<tr>
<td>Oil immersion</td>
<td>–</td>
</tr>
<tr>
<td>Pressurized apparatus</td>
<td>Purged / Pressurized</td>
</tr>
<tr>
<td>Increased safety</td>
<td>–</td>
</tr>
<tr>
<td>Intrinsic safety</td>
<td>Intrinsically safe</td>
</tr>
</tbody>
</table>

Nowadays powder filling and oil immersion are scarcely being used in the measurement and control technology and are not at all applied in gas detection. Pressurized apparatus, this means continuous purging e.g. with pressurized air, is a typical type of protection for major devices and cabinets. The standardized marking of an explosion protected device, e.g. Ex de IIC T4 or Class I, Div1, Group B, C, D, informs the expert about the applicability in the designated hazardous area.
Products for measuring and control technology, which have relatively low power consumption, can be designed very smart in respect to their explosion protection. Smart, because the product is designed such that even in case of a first or second failure it is ensured that neither sparks of sufficient energy nor surfaces of sufficient temperature can occur – so no risk of ignition.

Electrical discharges must have a certain minimum energy (ignition energy), otherwise they will not be able to ignite the most flammable mixture of a given flammable gas with air – hence, certainly no other arbitrary mixture of this gas in air can be ignited.

Also, for a given gas, the surface temperatures of electric or electronic components shall not exceed a certain temperature (ignition temperature).

Therefore, if the electronic circuits of a product are designed accordingly and the stored electric energy (i.e. effective capacities and inductivities) as well as electrical power (i.e. electrical current and voltage) are limited to certain maximum values, this electronic circuit cannot act as an ignition source – the product is said to be intrinsically safe.

There is an important accessory for this: When intrinsically safe current circuits lead into the hazardous area they need to be protected against too high power by so-called safety barriers. Safety barriers at least contain a fuse, resistors for current limiting and Zener diodes for voltage limiting.

Intrinsically safe products are marked by an “i”.

Their design is sophisticated, lightweight and simple – and intrinsically safe products can be maintained while energized. Cables may be disconnected and sensors may be replaced without zone declassification – because sparks and hot surfaces surely cannot exist.
The type of protection “flameproof enclosure” is the oldest of all, having been used in the early mining industry since the beginning of last century (the marking “d” refers to the German origin of this way of explosion protection). Compared to the protection type intrinsic safety a flameproof enclosure is a heavy and purely a mechanical method to avoid the ignition of an explosive atmosphere:

Simply let the explosion take place in the interior of the enclosure and reliably avoid a flashback. So housings of the protection type flameproof housing must be designed such that they will withstand the inner explosion pressure. The greater the housing’s volume, the higher is the possible explosion pressure, the more robust the housing shall be.

If flammable gases penetrate into the interior of the housing, one can assume that the housed electronic circuits (which also may produce sparks or have hot surfaces) will ignite the gases. On ignition the enclosure will withstand the explosion pressure, and the explosion pressure is released via joints. These mostly metallic joints with a certain minimum surface (with defined gap width and gap length) have an important function: Hot gases flowing along these joint paths are cooled down below their ignition temperature – a very effective flame extinguishing. With this type of standardized protection a potential flame in the enclosure’s interior cannot flash back into the hazardous area.

Flameproof housings are robust and heavy, and they are not allowed to be opened when energized. For maintenance an official hot work permission is necessary. The electrical connection of flameproof enclosed instruments can be made in three different ways:

1. **Rigid Conduit**: The electrical wires are run inside enclosed approved metal pipes. The pipes are directly screwed into the tapered NPT thread of the instrument. The complete conduit system is specially sealed and flameproof.

2. The cable is connected via an approved flameproof cable gland. Disadvantage: Explosion protection cannot be ensured by the manufacturer but only by the installer on-site.

3. The cable connection is done via an approved junction box with increased safety (“e”).
Also known as ATEX 95 (formerly ATEX 100a), mandatory in the European countries (EU) since 1st of July 2003, addressed to the manufacturers. Equipment and protective systems for the use in potentially explosive atmospheres need to fulfill the Essential Health and Safety Requirements (EHSR) which are assumed to be met when based on certain harmonized standards.

CE-marking for free trade within the European Union:

- Notified Body Number concerning quality
EU-requirements are met

Marking (according to ATEX):

- II 2 GD
- Type of potentially explosive atmosphere:
  
  G: Gas, vapour; D: dust
- Category
  I: Mining, II: other areas except mining
- Explosion protection:
  
  Ex ib IIC T4
  
  - Temperature class
  - Explosion group: I: Mining, II: other areas except mining for ia, ib, d and n: Subgroups IIA, IIB und IIC
  - Type of protection (here: intrinsically safe)
  
  Explosion protected equipment

EC-Type Examination Certificate:

- TPS 04 ATEX 1003X
  
  - X: Special conditions
  - U: incomplete Ex-component
  - Number of certificate
  - complies with the directive 94/9/EC
  
  Year of the certificate’s publication
  
  Notified Body having type-approved the equipment

Device categories and safety requirements:

<table>
<thead>
<tr>
<th>Device group</th>
<th>Category</th>
<th>Safety</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (Mining)</td>
<td>M1</td>
<td>very high</td>
</tr>
<tr>
<td></td>
<td>M2</td>
<td>high</td>
</tr>
<tr>
<td>II (other areas except mining)</td>
<td>1</td>
<td>very high</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>high</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>normal</td>
</tr>
</tbody>
</table>
Also known as ATEX 137 (formerly ATEX 118a), mandatory in the European countries (EU) since 30th of June 2006, addressed to employers and end-users concerning the minimum requirements for health and safety for workers in potentially explosive atmospheres.

Zone definition:

<table>
<thead>
<tr>
<th>Gas, vapour</th>
<th>Dust</th>
<th>Explosive atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>zone 0</td>
<td>zone 20</td>
<td>continuously, long periods or frequently</td>
</tr>
<tr>
<td>zone 1</td>
<td>zone 21</td>
<td>occasionally, likely to occur</td>
</tr>
<tr>
<td>zone 2</td>
<td>zone 22</td>
<td>infrequently and for a short period only</td>
</tr>
</tbody>
</table>

Selection of equipment (this table is the link between categories of the ATEX 95 and zones of the ATEX 137):

<table>
<thead>
<tr>
<th>Operation allowed for</th>
<th>Gas, vapour (G)</th>
<th>Dust (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Devices of category 1</td>
<td>in zone 0, 1, 2</td>
<td>in zone 20, 21, 22</td>
</tr>
<tr>
<td>Devices of category 2</td>
<td>in zone 1, 2</td>
<td>in zone 21, 22</td>
</tr>
<tr>
<td>Devices of category 3</td>
<td>in zone 2</td>
<td>in zone 22</td>
</tr>
</tbody>
</table>

Example: In zone 21, where explosive atmospheres caused by dust are likely to occur, the instruments to be used need to have a marking II 2D or II 1D.

Necessary measures:
- Assessment of the risk of explosion
- Classification of the hazardous area into zones
- Marking of the hazardous places by means of a triangular warning sign “Ex”
- Adequate safety measures
- Explosion protection document
- Competence of employees
- Criteria for a permit-to-work system for dangerous work

Guideline for risk reduction:
- Prevent the formation of explosive atmospheres, or, if this is not possible:
- Avoid the ignition of the explosive atmosphere, or, if this is not possible:
- Minimize harmful effects of explosions to a tolerable degree.
The term Safety Integrity seems to be something like a fashion in the technical-based and automatically operated safety technology. But it is not, and fixed installed gas detection systems are not exempted from this trend to classify protection systems by means of the so-called Safety Integrity Level (SIL) in respect to their reliability to activate a risk-reducing safety action.

- Wherever there is a technical risk for people, assets or environment it is necessary to gain a certain degree of safety by means of risk reducing measures. If such measures are realized automatically by electric, electronic or programmable electronic systems the central term is “functional safety”.
- Such systems, frequently called protective systems or safety relevant systems perform a safety function and need to be adequately reliable in respect to the actual risk.
- However, such systems can fail by any arbitrary failure. If they fail they must not remain in a dangerous (unsafe) state and need to be repaired instantly. This however implies that the occurrence of a failure is detectable at all.
- A high fraction of all the possible failures (which are identified by a so-called FMEDA) can be made detectable by failure monitoring (diagnostic facilities), so that the system in case of a detectable failure can be forced into the safe state, which is said to react fail-safe.
- Statistically there is a very small remaining fraction of accidental dangerous failures which cannot be detected automatically, the so-called dangerous undetectable or DU-failure, which might be seldom, but will impede the execution of the safety function.
- Setting the probability of the occurrence of a DU-failure into relation to all possible failures this will result in the so-called Diagnostic Coverage value $DC$ and the important Safe Failure Fraction $SFF$. Both these values must exceed certain percentages depending on the individual safety requirements.
- By ingenious system concepts (especially by redundancies), periodically repeated function proof tests and preventive measures the probability of the occurrence of a DU-failure can additionally be decreased.
- The remaining residual risk can be assessed statistically and classified. This results in four different safety integrity levels SIL1 to SIL4, where SIL4 is reflecting the highest reliability but is not established for gas detection systems, which are rather SIL2 and – by means of redundancies – SIL3 rated.
What to do in case of an alarm? Gas detection systems are designated to trigger alarms in sufficient time to inform the operator about the alarm condition and to perform counter measures for the prevention of a dangerous situation. This is mostly an automatism, but can also be achieved by establishing an alarm plan. It is in the operator’s responsibility to adequately react in case of an alarm.

The safety concept of a gas detection system always is: Detect dangerous gas, react and avert.

Main alarm
The exceeding of only one alarm threshold (main alarm threshold) is basically sufficient. By this the safe state is achieved by protecting the hazardous area (visible / audible alarm and evacuation) or by shutting off gas supply or by disable the ignition sources, call for use of personal protection equipment or breathing protection etc. This is a safe but rigorous, so to say uneconomic measure – the entire process is affected and shut-down.

Pre-alarm
This can possibly be avoided by means of a pre-alarm which is activated at lower concentrations than the main alarm threshold. With the pre-alarm automatic counter measures can be initiated which, if they are effective, will prevent the main alarm from being triggered, e.g. a pre-alarm can activate an effective ventilation so that the gas concentration stops rising and the main alarm threshold is not exceeded. This is ideal because: Via a pre-alarm a dangerous situation can be controlled without process shut-down. It is the operator’s interest to design counter measures so effective that the main alarm will most likely never be triggered: Properly designed gas detection systems will reach main alarm only seldom or never.

Fault condition alarm
Fault condition alarms indicate that the system is partly or entirely inoperative and in case of a gas release cannot react properly. Preventively the same measures need to be taken in case of fault condition as in case of a main alarm, since there is no gas detection system at all. With this philosophy a safe condition is achieved best.
A gas detection system’s reliability is not only depending on the properties and performance of the equipment, but also depending on installation, operation and maintenance – and especially the proper positioning of sensors. Naturally, sensors can only detect a gas when the sensor is within the gas cloud. Incorrect sensor positioning results in a useless gas detection system.

Gas leaks can arise e.g. when cold liquefied and/or pressurized gases are released into the ambient air, and get mixed with it. Their concentration decreases, and the gas dispersion depends more on the current temperature conditions and ambient air convection than on the density of the pure gas.

Three Rules of Thumb:
- There are only three flammable gases which are considerably lighter than air: Hydrogen (H\textsubscript{2}), Ammonia (NH\textsubscript{3}), and Methane (CH\textsubscript{4}). Commonly mixtures of these gases rise up.
- Vapours of flammable liquids are always heavier than air – they flow downwards as long as they are not disturbed by air convection.
- Independent of the density of the pure gas, gas concentrations of less than 1000 ppm in air virtually have the same density than air. Dispersion of concentrations like this will rather follow the current temperature profile and air convection.

Positioning strategy:
Having the sensors as close as possible placed at the potential leak surely is the optimum way. Leaks may arise from pumps, valves, flexible tubes and their connections, flanges, shut-off devices, bellows, etc. If such locations cannot easily be identified, sensors need to be distributed over the entire hazardous area (area monitoring). It is essential that the target gas always can reach the sensor at operational conditions within a given time interval. The local conditions of the individual hazardous areas are so very different that there are no regulatory standards where to place a sensor, but useful guidelines exist (e.g. the EN 50073 or IEC 60079-29-2).
In a first approach gas sensors do not measure gas concentrations directly: Electrochemical sensors measure electron flow changes, catalytic bead sensors measure resistance changes, and IR-detectors measure changes of IR-radiation intensity in the near infrared. These changes always refer to the normal condition (clean air) which is called zero point because no target gas is present. Only by calibration it is possible to correlate a certain gas concentration to a certain output signal, resulting in a gas detection instrument.

Calibration is extremely important. Obviously, gas detection instruments cannot measure properly as long as they have not been calibrated properly. While zero-calibration is rather simple because ambient air can mostly be used for this purpose, calibration of the sensitivity (called span-calibration) is not so trivial.

For the same reason that electrochemical sensors can detect reactive gases, they have to be calibrated using reactive gases. But unfortunately a lot of reactive gases also react with (moist) material surfaces and plastics. Although from the aspect of safety it is recommended to perform the span-calibration with the target gas (the gas which shall be detected) there are several reasons to use an easy-to-handle surrogate test gas for cross-calibration. If a variety of gases or vapours shall be detected by only one sensor, the instrument has to be calibrated for the substance the sensor is the least sensitive to. Thereby, the gas detector is calibrated to the safe side, because all gas concentrations are either measured properly or as too sensitive. The sensor’s sensitivity for certain gases cannot be calculated from gas specific data, but can only be determined by applying the gas and evaluate the response.

To achieve good measuring performance, calibration should be performed as good as possible under the expected conditions during operation.

Calibration chamber for flammable liquids
To obtain a given %LEL concentration of flammable vapours it is recommended to use a calibration chamber, where a certain calculable amount of liquid (e.g. 100 microlitres) has to be inserted. After complete evaporation a concentration of e.g. 50 %LEL is formed which can be directly applied to the sensor.
Since gas detection instruments and systems are products of safety technology for industrial applications they need to comply not only with statutory requirements (e.g. electrical safety, explosion protection, electromagnetic compatibility) but also with further requirements such that even in harsh industrial environments the product’s quality and reliability of alarming will sustain.

Standards concerning explosion protection:
Design requirements make sure, that devices will not act as a source of ignition. World-wide accepted standards are issued by e.g. CENELEC (ATEX), IEC, CSA, UL, GOST, etc.

Electromagnetic compatibility acc. to EN 50 270:
Test standards ensure that devices do not produce wire bound or radiated disturbances, and especially, that they are not negatively influenced by wire bound disturbances (surges, bursts) or high frequency emissions (80 MHz to 2 GHz at field strengths up to 30 V/m), and that they withstand electrical discharges without being affected in respect to their reliability. The relevant test standards are based on the series IEC 61000.

Climate, vibration and impact, e.g. acc. to IEC 60028:
Dry and damp heat temperature cycles (up to 70 °C, including condensation!) over several days and cold test. During these cycles, sporadic function tests and insulation resistance tests with high voltage are performed. Vibration test up to the 4-fold gravity for 90 minutes each axis at the determined resonance frequencies have to be passed without affecting proper function.

Measuring performance:
A certain measuring performance has to be met even under extreme environmental conditions (temperature, pressure, wind speed, relative humidity, vibration, etc):
EN 61 779 / EN 60079-29-1 – for flammable gases/vapours
EN 45 544 – for toxic gases and vapours

Digital communication acc. to EN 50 271:
Transmitter and controller nowadays are mostly microproces- sor-controlled. Hardware and software need to comply with certain requirements concerning the system’s reliability.

Shipping approvals:
Requirements of the so-called classification societies e.g. Det Norske Veritas (DNV), Lloyds Register of Shipping (LRS), Germanischer Lloyd (GL), Bureau Veritas (BV), etc.
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.
Sensors for the detection of gases and vapours are transducers making use of certain properties of gases for the conversion into a suitable electrical signal. Especially three measuring principles have become mainstream in the recent decades of industrial gas detection: Electrochemical sensors, catalytic bead sensors and infrared sensors.
In almost every industrial application flammable substances are used. Equipment installed in these areas needs to be explosion protected and must be approved and certified for this purpose.

With suitable safety concepts, high availability and failure resistance, gas detection systems turn into reliable protection systems.