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## **GASES**

A gas (Gr.  $\kappa\alpha\omicron\zeta$ , chaos, atmosphere) is a substance showing such a large tendency to expand that, no matter how small quantity there is, it fills the entire container (where the electromagnetic forces of contact prevent further expansion, although sometimes gas diffusion through the wall is important), or it expands as much as the gravitational forces prevent any further expansion.

The perfect gas model (PGM), is the simplest full model for the thermodynamic behaviour of a gas; it combines the ideal gas model  $pV=mRT$ , which applies to all gases at low pressure, and the perfect thermal model,  $\Delta U=mc_v\Delta T$ , which is a good approximation for no too large temperature excursions.

Gases may be procured bottled in several ways:

- As compressed gas at high-pressure, usually at 20 MPa (as for N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, Ar, He, H<sub>2</sub>).
- As compressed gas at medium-pressure (for small needs).
- As liquefied gases at medium-pressure (as for commercial butane, propane, refrigerant fluids and carbon dioxide).
- As refrigerated liquefied gases (CO<sub>2</sub> and N<sub>2</sub>O, due to their critical temperature).
- As cryogenic liquids at low pressure over the atmosphere (as for liquid N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, He, H<sub>2</sub>).

- As gases dissolved in a liquid (acetylene,  $C_2H_2$ , is bottled dissolved in acetone,  $CH_3COCH_3$ , soaked in a porous filling).

Notice that liquefied gas bottles can deliver liquid from the bottom (instead of gas from above) when provided with a siphon (a tube that connects the head valve with the liquid; as in spray cans and soda siphons). Liquid can be also deliver by placing the outlet valve at the bottom (e.g. by holding the bottle upside down, as when refilling propane gas lighters).

Just for small laboratory tests, in-situ production is often preferable:  $H_2$  and  $O_2$  may be produced by water electrolysis,  $CO_2$  by dripping an acid over a carbonate, and  $CH_4$  and  $C_2H_2$  by dripping water over  $Al_4C_3$  or  $Ca_2C$ , respectively. Intermediate gas storage is usually achieved by a hydraulic seal as in a gasometre. Major manufacturers of industrial gases are The Linde Group (Germany), Air Liquide (France), and Praxair (USA).

### Natural gases

All natural gases are gaseous mixtures of several pure chemical components (sometimes holding solid or liquid particles in suspension). By far the most apparent gas in nature is air in the Atmosphere surrounding the Earth.

Air was thought to be a pure substance up to the 17th century, when [van Helmont](#), a disciple of Paracelsus, identified around 1640 carbon dioxide as 'gas sylvestre' (he coined the word 'gas' too); detailed studies on carbon dioxide, however, were first presented by [J. Black](#) in 1756, who produced it from limestone by heating or treating with acid, and called it 'fix air'. In 1766 H. Cavendish isolated what was called 'flammable air' ( $Zn(s)+H_2SO_4(aq)=ZnSO_4(s)+H_2(g)$ ), and in 1770 J. Priestley isolated many more gases ( $O_2$ ,  $NH_3$ ,  $CO$ ,  $NO$ ,  $NO_2$ ,  $SO_2$ ) by using mercury instead of water as hydraulic seal, since many gases dissolve in water. Air composition is nearly constant all around the globe up to some 80 km; once filtered of suspended particles, and dried (removing its water vapour content), nearly 99% of its molecules are nitrogen (78%) and oxygen (21%), the rest being mainly argon (1%), carbon dioxide (0.04%), and other minor gas constituents. Water vapour in the air varies a lot with latitude, longitude and altitude, from 0..4%, with an average of 2% at sea level; although in such small proportion, water-vapour controls most meteorological processes, and is important to engineering (e.g. air conditioning, drying, humidification, condensation).

Nowadays the term natural gas refers exclusively to a gaseous mixture consisting mainly of methane trapped below ground, used extensively as a fuel (see below).

### Industrial gases

Leaving natural air aside (used by all living beings for respiration and cooling), the gas with largest share in the market place is natural gas (used as a fuel and chemical stuff), the second oxygen (used in combustion and medicine) and the third nitrogen (used as a chemical stuff, as an inert atmosphere and as a coolant; 85% of world production is by cryogenic distillation, the rest, of lower quality, mainly by Gases

hollow-fibre polymer membrane selective permeability). Other industrial gases are produced from chemical reforming ( $H_2$ , used as a chemical stuff, as a rocket fuel and in the food industry), or from industrial waste (as  $CO_2$ , used in the food and beverage industry, as a coolant, as a solvent, in welding and fire-fighting).

Under the Kyoto Protocol, there are six gases that count towards an emissions reduction target:  $CO_2$ ,  $CH_4$ ,  $N_2O$ , HFC (hydro-fluorocarbons), PFC (phosphor-fluorocarbons) and  $SF_6$ ; these last three are man-made and have extremely high global warming potentials.

### Gas separation

At industrial level, gas separation from natural mixtures started in 1890s with the cryogenic distillation of air, still a major industrial process, although adsorption and absorption processes, and nonporous polymeric membrane separation, are taking over. First water vapour, and then carbon dioxide, are condensed and removed, before air is liquefied.

High purity  $O_2$ ,  $N_2$  and Ar are produced by the separation of air through the use of cryogenic distillation and adsorptive processes. Noble gases can be obtained by air separation, as for argon, but helium extraction cannot compete in price with that obtained from some natural-gas fields close to uranium ores (there is up to 8% of He in some USA gas fields). The second commercial process to separate the air components is based on preferential adsorption by suitable materials like silica-gel, activated carbon, zeolite molecular-sieve, and some other porous solids. The adsorbed species is released and the adsorbent regenerated by the application of heat (temperature swing adsorption, TSA), pressure (pressure swing adsorption, PSA), or vacuum (vacuum swing adsorption, VSA), or a hybrid like VPSA. Oxygen with >90% purity is produced from air in a VSA-plant using a zeolite molecular-sieve adsorbent to remove nitrogen, carbon dioxide, and water from a stream of compressed air, and, when the sieve is saturated, a vacuum pump removes the adsorbed gases, enabling the sieve to be reused.

High purity  $H_2$  and CO are produced from synthesis gas (obtained by reforming fossil fuels with water vapour and air), with gas separation by selective absorption or cryogenic distillation.

### Gas analysis

Knowing the composition of gases (and of liquids and solids, and of multiphase systems) is important for their utilisation, and may even be critical for survival (e.g. is an atmosphere breathable? explosive?)

We focus in the analysis gases in the gas phase, although in many cases one wants to know the composition of dissolved (or absorbed and adsorbed) gases (e.g. dissolved gasses in water or in blood, trapped gases in ice or in bread...). In the latter case, one has to first proceed to the outgassing from the liquid or solid. As historical and modern practice in gas analysis, we may consider:

- Analysis of fresh air from the atmosphere (e.g. to know its main constituents, to measure humidity, pollution...).

- Analysis of other ‘natural’ gases, like our exhalation gas, flue gases from combustion, fuel gases and vapours, and fuel/air mixtures...
- Analysis of gases in chemical and biological processes (e.g. brewing, distillation, synthesis...).

Except for new synthetic gases, where atomic characterisation and steric molecular behaviour must be researched, the ultimate accuracy in gas analysis is by comparison with gas standards (pure, and calibrated mixtures) provided by well-known industrial or institutional suppliers (e.g. [NIST](#), [NPL](#)).

Gas analysis is relatively simple because bulk characterisation of a single phase is implicit. When condense matter is present, either in bulk or dispersed (e.g. aerosols), the analysis is more complicated. In condense matter, besides bulk analysis, one may be interested on surface-composition (often quite distinct to that of the bulk phase). In the latter case, one may still consider different depths in the interphase: monolayers (monoatomic layers of about 0.1 nm, nano-surface (up to 10 nm), nano-film (10..100 nm), micro-film (100..1000 nm), and bulk (>1 mm thick). The study of the separation, identification, and quantification of the chemical components of natural and artificial substances is the realm of [Analytical Chemistry](#). Chemical analysis, i.e. composition identification, may be done by pure physical means (e.g. by densitometry, refractometry...), by pure chemical means (e.g. exposing the sample to different reactives or absorbers), or more commonly by physico-chemical means, mainly spectroradiometry, and electrochemistry.

Gas analysis may be dangerous and difficult if we have no idea of its composition; will the sample explode (or get distorted anyway) when strongly shaken, or illuminated strongly, or when in contact with our instrumentation? When some main constituents are known to occur, the analysis gains accuracy (and may be easier) if the known component is removed; this is particularly important in the case of water vapour, which may condense on the instruments, or whose rich molecular behaviour may complicate spectral analyses).

A gas may also be called ‘vapour’ if it can easily condense by changes in temperature, pressure, or composition); e.g. water vapour in the air, gasoline vapours, ammonia vapours... In other contexts, a vapour is a gas in equilibrium with its condensed phase, but this may be tricky for mixtures (e.g. in a closed container partially filled with water, nitrogen gas is in equilibrium with dissolved nitrogen, and nobody calls it a vapour).

Gas composition is usually stated in molar fractions,  $x_i = n_i / \sum n_i$  (coincident with volume fractions), although conversion to mass fractions is not difficult. According to concentration range, one may distinguish:

- Main components, with molar fractions of order one, i.e.  $x_i = 0.1..1$ .
- Secondary constituents (not main, not trace).
- Trace components, with or  $x_i < 10^{-3}$  (in engineering; in other sciences may be  $x_i < 10^{-6}$ , i.e. <1 ppm).  
Trace gases are of interest in breathing (from pleasant odours to [lethal vapours](#)), as markers and

contaminants of other gases (e.g. [mercaptans](#) in fuel gases), or as [residual gases](#) in vacuum chambers.

From a general environmental point of view, focusing on a breathable atmosphere, one may consider (in order of descending concentrations, aside of the almost inert nitrogen (N<sub>2</sub>, not usually measured but considered as 'the rest'), the following gases of interest:

- Oxygen (O<sub>2</sub>). About 21 % molar in fresh air, key to breathing and combustion. It is usually measured with an electrochemical contact probe. Other method makes use of the paramagnetic property of O<sub>2</sub>; it consists on two platinum hot wires in a Wheatstone bridge, both exposed to a small flow of test gas, but one of them under a magnetic field that concentrates the oxygen in the gas mixture and increases its thermal conductivity. Before a person enters a suspected closed space (e.g. a cellar, a cave, a cargo bay in a ship, another compartment in a space station...) one should check there is enough oxygen (and not so much noxious gases;  $x_{\text{CO}_2} > 0.1$  may be fatal in a few minutes, by [hypercapnia](#)).
- Water vapour (H<sub>2</sub>O). About 1 % in fresh air at sea level, important in meteorology, air conditioning... Many methods are used in current [hygrometry](#) practice: IR absorption, electrical capacity of a moisture-sensitive dielectric, wet-bulb thermometer, dew point thermometer, absorption in a hygroscopic salt...
- Carbon dioxide (CO<sub>2</sub>). About 0.04 % in fresh air, important in combustion and breathing (and in climate change). It is usually measured by IR absorption.
- Fuel gases and vapours. Detectors are commonly known as [explosimeters](#), and usually measure electrical resistance of a hot platinum wire (similar to those used in hot-wire anemometry) where combustion occurs locally (the sensor is located inside a flame arresting mesh). They are usually calibrated (using test mixtures) to give an early warning at a about half the lower [flammability limit](#). Notice that they rely on oxygen in the air to burn the fuel gas, so they cannot work in inert atmospheres (and should not be operated in pure-oxygen atmospheres!). For precise analysis, other sensors and instruments are used.
- Flue gases. Carbon monoxide, volatile organic compounds, and nitrogen oxides, emitted from combustion processes.
- Organic and inorganic gases and solvent vapours used in industrial processes; e.g. for cleaning purposes, water treatment, manufacturing, refrigeration, etc.

## Sampling

Type of analysis according to sequence of events

- Non-extractive in-line and in-situ simultaneous analysis (gives  $x_i(t)$  at the imaging point in the system).
- Extractive:
  - Bleeding. In-line analysis, with or without chromatographic separation, of the bled. Gives  $x_i(t)$  at the sampling point in the system, but may be modified by the sampling probe.
  - Sampling, with a sample collector (is the sample representative?), sample store (is the sample stable?), and sample analysis in the lab.

### Sample collection (gas bottles)

When immediate analysis of gas is not convenient, a certain amount of gas is collected in a recipient, either flexible (bags) or rigid (bottles), stored, and transported to a lab for analysis. A bottle is usually made of glass or a similar material (quartz, plastic). A flask is a more generic container. A vial is a test-tube (typically of 10 mL capacity), or a miniature bottle (as used in medical injection). A gas bottle is an intermediate gas holder, used to later supply standard samples to analytical instruments.

Notice, however, that there are gases not amenable to storage, which must be analysed in a short time, or without containment; e.g. gases that decompose with time like some nitrogen oxides, gases too reactive or at very high temperature (e.g. within a flame). Sample preparation is the most error-prone and labour-intensive task in the analytical laboratory.

To avoid contamination, the obvious way is to collect just the gas to analyse, either in an empty bag or in an evacuated bottle. One of the older (and cleaner and easier) ways to hold (and manipulate) a gas sample is to use an upside-down glass bottle initially full of water and partially submersed open-mouth in a water bath: a gas can be easily introduced in the bottle through a flexible tubing, and get trapped inside, displacing some water by buoyancy, and the hydraulic stop is most convenient (to have an air-tight joint is very difficult). Stoppers in bottles and tubes are usually made of rubber. Metal crimps are often used to secure the rubber stopper. A non-return valve may simplify sample collection by just opening the valve in an evacuated rigid container (or in a pre-loaded flexible or elastic bag).

Sometimes, instead of using evacuated bottles, they are pre-filled with a well-defined over-pressurised gas (say at 200 kPa and 25 °C). Bottles pre-filled with different-composition of a calibrated gas are used to enhance accuracy in later analysis. Typically, bottles with pre-filled gas can maintain gas composition to 1 ppm for more than a month. The overpressure facilitates gas extraction (e.g. with a manual syringe).

Comentado [i1]:

If dismountable joints must be used in gas pipes (e.g. to place probes and other equipment), special threads should be used (e.g. gas threads like [BSP](#), where thread dimension do not refer to thread diameter but to the internal diameter of the gas tube). The case of vacuum piping is still more complicated.

### **Analytical techniques**

There are many new analytical techniques to find the chemical composition of a gas, among which we have electroanalytical methods, gas chromatography, mass spectrometry, and radiation spectrometry.

[Electroanalytical methods](#) measure the potential (volts) and/or current (amps) in an electrochemical cell containing the analyte. These methods can be categorized according to which aspects of the cell are controlled and which are measured. The three main categories are potentiometry (the difference in electrode potentials is measured), coulometry (the cell's current is measured over time), and voltammetry (the cell's current is measured while actively altering the cell's potential).

Gas chromatography (GC) is used to separate mixtures (gaseous or liquid) into individual components using a temperature-controlled capillary column; smaller molecules with lower boiling points travel down the column more quickly than larger molecules with higher boiling point, producing a spatial separation.

Mass spectrometry (MS) is used to identify the various components by measuring the mass-to-charge ratio of molecules using electric and magnetic fields. Each compound has a unique mass spectrum that can be compared with mass spectral databases and thus identified, and quantified by comparison with standards.

Gas chromatography - mass spectrometry (GCMS) is a technique for the analysis of organic compounds, either gases, liquids, or solids. For liquids, the sample is directly injected into the GC. For gases, gas tight syringes are used to transfer the gaseous components directly into the GC. For solids, the analysis is carried out either by solvent extraction, outgassing or pyrolysis.

[Spectroscopy](#) measures the interaction of the molecules with electromagnetic radiation, either absorbed, emitted, or dispersed. Although initial developments were in the visible band of the spectrum (Rb and Cs were discovered in 1866 by Bunsen and Kirchhoff using flame emission spectrometry), nowadays most radiometric techniques work in the [infrared band](#), since gases at moderate temperatures show more characteristic features at frequencies related to molecular rotation and vibration, rather than at the higher frequencies associated to electron-level changes. Instead of dedicated gas detectors, spectroscopic techniques like the Fourier transform infrared spectrometers ([FTIR](#)) can render simultaneous concentrations for tens of components. The FTIR is a radiation absorption technique that, instead of using a monochromator and measuring absorption at a given frequency, shines a wide spectral band IR beam on a transparent gas cell (see Fig. 1), measures absorption from this spectral combination, then changes in a known way the spectral distribution of the source (using a Michelson's interferometer), and measures absorption again. This process is repeated many times, and afterwards, a computer takes all these data and works backwards to infer what the absorption is at each wavelength.

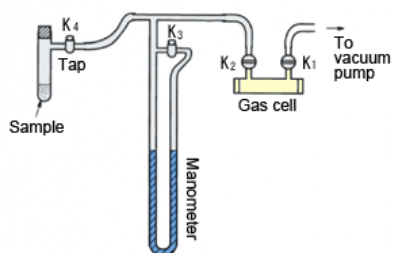


Fig. 1. Filling a gas cell for FTIR ([Shimadzu](#)). Open taps K1, K2, and K3 to evacuate the gas flow line, and close K3; then, close K1 and gradually open K4 to allow the sample to flow into the gas cell. Watch the manometer and close K4 when the appropriate pressure is reached. Finally, close K2 and remove the cell to perform the measurements. The cell has parallel IR-windows made of KBr or KRS-5 (thallium bromide-iodide).

### The old Orsat analyser

The [Orsat gas analyser](#), developed by H. Orsat in 1873, measures the amount of CO<sub>2</sub>, CO, and O<sub>2</sub>, in a sample of flue gases from the combustion of a fossil fuel.

The apparatus consists of a burette (surrounded by water maintaining constant temperature), upward connected by glass capillary tubing to a set of glass bottles filled with absorbent solutions, and connected downward to a levelling bottle containing a saturated NaCl solution (which do not absorb any flue gases) and open to the ambient to enable readings to be taken at constant pressure. The operation is as follows:

- Fill with a dry and clean sample. Air in the apparatus is first expelled by opening the three-way stop cock and, with the three valves to the absorption pipettes closed, rising the levelling bottle. Then the three-way stop cock is rotated and flue gas is admitted in the burette by lowering the levelling bottle. The flue gas enters through a desiccant (e.g. CaCl<sub>2</sub>) to get rid of its water vapour content. This procedure can be repeated a couple of times to better get rid of any air inside.
- Take a measured sample. The levelling bottle is adjust to have a precise sample amount, usually 100 mL, and the three-way stop cock is closed.
- Absorb CO<sub>2</sub> gas in a KOH solution. The valve in the absorption pipette having a potassium hydroxide solution (about 0.3 kg per litre of water) is opened, and the flue gas in the burette is forced to enter by raising the levelling bottle. By repeatedly raising and lowering the levelling bottle, the gas is brought into intimate contact with the pipette KOH solution, which absorbs the CO<sub>2</sub> gas completely. Then the residual gas amount is measured in the burette by equilibrating the brine level with the levelling bottle (to recover ambient pressure). The lost volume of gases is the CO<sub>2</sub> volume fraction.
- Absorb O<sub>2</sub> gas in a pyrogallol solution. The same procedure is then repeated with the alkaline solution of [pyrogallol](#) (benzene-1,2,3-triol, C<sub>6</sub>H<sub>6</sub>O<sub>3</sub>), prepared by dissolving 0.4 kg of pyrogallic acid in 1 L of the KOH solution above. The further decrease in levelled volume gives the volume fraction of oxygen.
- Absorb CO gas in a cuprous chloride solution. Finally, the third absorption pipette, containing a [CuCl](#) ammoniacal solution (prepared by adding 0.25 kg of cuprous chloride and another 0.25 kg of ammonium chloride, to 750 mL of water), is used to obtain the volume fraction of carbon monoxide.
- The percentage of nitrogen is obtained by the difference.

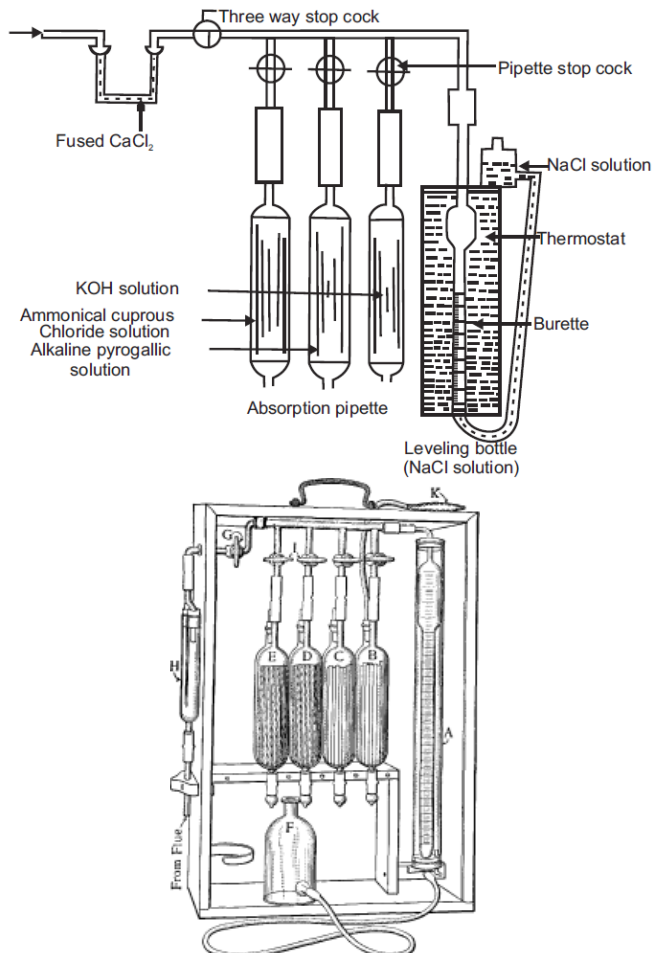


Fig. 1. Two sketches of the Orsat gas analyser ([Wiki](#)).

Notice that the order of absorption is important, that this analyser cannot be very accurate, that reagents get saturated, and that it only measures the three quoted gases. Manufacturing of Orsat analysers died out in the 1960s, being replaced by gas chromatography.

Other [combustion instrumentation](#) is presented aside.

### Dry air

Air must be dried in many industrial applications where vapour condensation cannot be allowed, or to avoid the growth of microorganisms. Water can be removed from air by absorption by hygroscopic chemicals recycled offline, by adsorption on some molecular sieves recycled alternatively (e.g. pressure swing adsorption, PSA), cold condensation, etc. Table 1 presents one of the several standard

compositions in use. In practice, the composition of dry air varies very little with latitude, longitude and altitude, because the atmosphere is well stirred globally (it is an air layer heated from below), but may show sizeable local variations. In secular terms, the major change is in CO<sub>2</sub> concentration: it was 0.030% by volume in 1900, 0.038% in 2007, and projections for 2050 are 0.100% in the business-as-usual model, and 0.050% in the most ecological prospect.

Table 1. ISO 2533 Standard dry air composition (sea level).

Gas	Chemical Formula	Percent by Volume
Nitrogen	N <sub>2</sub>	78.084
Oxygen	O <sub>2</sub>	20.9476
Argon	Ar	0.934
Carbon Dioxide	CO <sub>2</sub>	0.0314
Neon	Ne	0.0018
Helium	He	0.000524
Methane	CH <sub>4</sub>	0.0002
Krypton	Kr	0.000114
Hydrogen	H <sub>2</sub>	0.00005
Xenon	Xe	0.000009

## N<sub>2</sub>

[Basic thermodynamic data](#) for nitrogen can be found aside. [Nitrogen](#) was first isolated in 1772 by D. Rutherford, who called it 'noxious air', distinguished it from Black's 'fixed air' (CO<sub>2</sub>); Lavoisier, who put at that time most current chemical names, called it 'azote' (lifeless); the word nitrogen was coined in 1790 from the ancient word nitron, which referred to natural mixtures of niter (KNO<sub>3</sub>) and natron (Na<sub>2</sub>CO<sub>3</sub>). It is used as a chemical feedstuff in the fertiliser, pharmaceutical and explosive industries, as a cryogenic refrigerant ( $T_b=77$  K), and as an inert replacement for air where oxidation is undesirable.

## O<sub>2</sub>

[Basic thermodynamic data](#) for oxygen can be found aside. [Oxygen](#) was first isolated in 1774 by J. Priestley; the name oxygen was coined in 1777 by Lavoisier. It is used in breathing of all animals and plants, most combustion processes (either as component in the air, or pure like in oxy-cut torches and cryogenic rockets), and other industrial red-ox reactions (smelting of iron ore into steel consumes about 55% of world commercially produced oxygen).

## CO<sub>2</sub>

[Basic thermodynamic data](#) for carbon dioxide can be found aside. [Carbon dioxide](#) was the first gas to be described as a discrete substance, in about 1640 by [van Helmont](#), based on the new gas that appear when burning charcoal in a closes vessel; detailed studies were carried out by J. Black in the 1750s, when heating calcium carbonate under vacuum ( $\text{CaCO}_3(\text{s})=\text{CaO}(\text{s})+\text{CO}_2(\text{g})$ ), what he called 'fixed air'. CO<sub>2</sub> is the main exhaust gas produced in combustion, being the main contributor (after the innocuous water vapour) to global warming (see Dry-air composition, above). CO<sub>2</sub> is used in the food industry (carbonated beverages), as an inert gas, as a refrigerant, as a supercritical solvent, and as the building block of living matter by plants in the photosynthesis process.

CO<sub>2</sub> was first liquefied (at elevated pressures) in 1823 by Humphry Davy and Michael Faraday. In 1983, snow of solid CO<sub>2</sub> was first obtained. This [dry ice](#) sublimates at  $-78\text{ }^{\circ}\text{C}$  at 100 kPa (skin contact for more than a second produces blister frostbite, and storing dry ice in closed containers like thermos produce explosion and shrapnel). CO<sub>2</sub> properties vary a lot with temperature (e.g. Fig. 1).

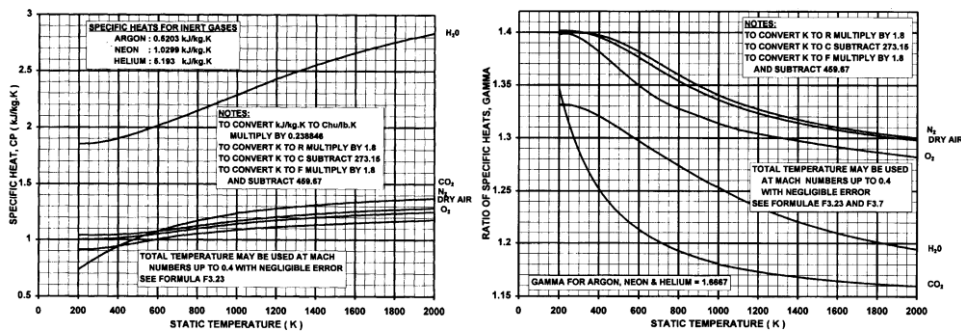


Fig. 1. Change of thermal capacity and thermal capacity ratio with temperature.

Carbon dioxide is present in the atmosphere (0.04% molar), in some ground cavities and water sources, and as by-product of many chemical processes like combustion, respiration, fermentation, etc. CO<sub>2</sub> was discovered by J. Black in 1754 who named it 'fixed air' or un-breathable air (noticing that both a lighted candle and a mouse died under a gas-filled bell). Industrial production may be based on chemical processes (e.g. production of H<sub>2</sub> and NH<sub>3</sub> liberates a lot of CO<sub>2</sub>), biological processes (from sugar or starch fermentation), or from natural underground depots of volcanic origin (some with >90% CO<sub>2</sub>, found in USA and in Europe, e.g. at Répcelak in Hungary; geothermal carbon dioxide is found in numerous locations).

Used by plants for photosynthesis, to gasify carbonated drinks, as a protective atmosphere (non-flammable and non-oxidant), as a supercritical fluid extraction media (e.g. to decaffeinate coffee), as a refrigerant, as a chemical stuff for methanol and urea synthesis, as a fluidiser to help crude-oil extraction in some wells (there are several CO<sub>2</sub> pipelines, several hundred km long, being used in the USA for that purpose), etc. It is handled bottled at high pressure, in a state that depends on ambient temperature (Fig. 2). Best bulk transport is as a supercritical fluid by pipelines at high pressure (around 10 MPa); transport by sea, in refrigerated tankers at around  $-20\text{ }^{\circ}\text{C}$  (2 MPa) is more expensive.

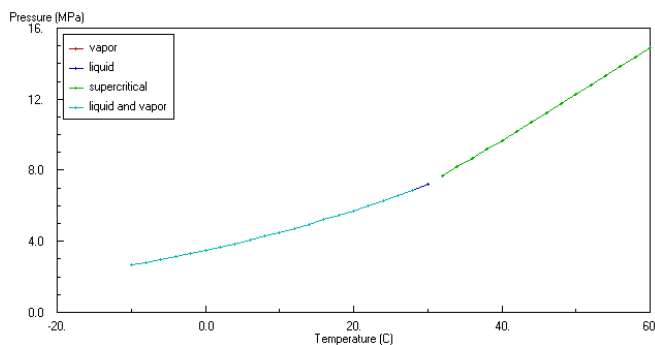


Fig. 2. Internal state in a CO<sub>2</sub> bottle of 0.02 m<sup>3</sup> with 12 kg of CO<sub>2</sub>, as a function of temperature.

Chemistry. Linear molecule: O=C=O. Carbon dioxide dissolves slightly in water to form a weak acid called carbonic acid, H<sub>2</sub>CO<sub>3</sub>, what explains why water, which normally has a neutral pH of 7 has an acidic pH of approximately 5.5 when it has been exposed to air. Pure CO<sub>2</sub> can be easily obtained by mixing vinegar and yeast powder.

## C<sub>2</sub>H<sub>2</sub>

[Basic thermodynamic data](#) for acetylene (ethyne) can be found aside. [Acetylene](#) is a colourless, highly flammable gas (may decompose explosively), used in the chemical synthesis (80%), welding with the oxy-acetylene torch (20%), and in chemical analysis, first obtained and named by Berthelot. Acetylene is produced from CaC<sub>2</sub> and water, or by hydrocarbon cracking, or by partial oxidation of natural gas. CaC<sub>2</sub> was first obtained in 1892 while searching for aluminium synthesis, by passing an electric arc through calcinated limestone (CaO) and coal tar. Acetylene can be produced in situ, but it is usually traded in high-pressure bottles, in liquid form, dissolved in acetone (and stabilised within a solid porous material) since pure acetylene may decompose explosively if  $p > 205$  kPa (for that reason the typical oxy-acetylene torch is not used for underwater work below 10 m depth, being substituted by a H<sub>2</sub>/O<sub>2</sub> torch).

The oxy-acetylene torch is the common tool for manual cutting and welding, because of its high heating power and high combustion temperature, 3500 K, the maximum of any fuel. A typical workshop bottle of 40 litres, at 1.5 MPa, yields some 6 m<sup>3</sup> of acetylene at room conditions (the flow rate should not be higher than 1 m<sup>3</sup>/h to avoid acetone carry-over). The volume within the bottle is typically filled as follows: when 'empty' (i.e. before the C<sub>2</sub>H<sub>2</sub> charge), 20% is occupied by the porous material (e.g. calcium silicate with a binder), 40% by the liquid acetone solvent, and the remaining 40% by room-temperature solvent vapour (vapour pressure of acetone at 25 °C, 30 kPa); when fully loaded, 20% is occupied by the porous material, 68% by the liquid solution of acetone and acetylene, and the remaining 12% by room-temperature solution vapours (basically acetylene gas) at about 1.5 MPa. A given commercial-bottle has the following characteristics: C<sub>2</sub>H<sub>2</sub> bottle of 41 L, 0.229 m diameter and 1.112 m height, with a tare of 16.3 kg, filled to 1.8 MPa at 15 °C, containing a liquid solution with 7 kg of C<sub>2</sub>H<sub>2</sub> (yields 8.0 m<sup>3</sup> at 100 kPa, 0 °C) plus 16 kg of C<sub>3</sub>H<sub>6</sub>O plus 10 kg of solid filling; total weight 16.3+7+16+10=50 kg. The empty space is to allow for thermal expansion (up to 50 °C, pressure must not rise over 20 bar; the hydraulic test on raw bottles is

at 55 bar). Bottles should always be kept upright to prevent acetone entrainment during operation (if transported on their side, it will take up to 24 hours for the contents to re-stabilize once vertically positioned). A double pressure gauge is used to indicate the cylinder supply pressure entering the regulator, and the delivery pressure from the regulator to the hose. Gas content should not be measured by pressure (they are not linearly dependent) but by weight.

A volume of acetone dissolves 25 volumes of  $C_2H_2$  gas at 0 °C and 100 kPa, increasing 4.7% the liquid volume (thus, 16 L of acetone accepts  $16 \cdot 25 \cdot 15 = 6 \text{ m}^3$  of standard gas ( $C_2H_2$  at 0 °C and 100 kPa) at 1.5 MPa, with a  $4.7 \cdot 15 = 70\%$  volume increase (from 16 L to 27 L). Technical grade acetylene may have a garlic-like odour due to the presence of impurities (traces of ammonia, hydrogen sulphide and phosgene, that make it nose-detectable at >600 ppm). It is not toxic below its LEL of 2.5%, but at 35% it is toxic (unconsciousness after 5 minutes), and at 40% lethal.

### $C_3H_8$ , $C_4H_{10}$ and LPG

[Basic thermodynamic data](#) for pure components can be found aside. [LPG](#) (liquefied petroleum gas) are several commercial petroleum-derivative mixtures (gaseous at ambient temperature, but handled as liquids at their vapour pressure, which depends on temperature, and may be in range 0.2..2 MPa), mainly constituted by propane, n-butane, iso-butane, propylene, and butylenes, with composition widely varying according to use.

For domestic applications, LPG may range from nearly 100% propane in cold countries, to only 20..30% propane in hot countries; e.g. 100% in UK, 50% in the Netherlands, 35% in France, 30% in Spain, 20% in Greece. In Spain, the traditional bottle for domestic use (UD-125) holds 12.5 kg of commercial butane (56% n-butane, 25% propane, 17% iso-butane, 2% pentane, 0,1 g/kg  $H_2O$  and 1 mg/kg mercaptans, with  $T_b = -0.5 \text{ °C}$  and  $\rho_L = 580 \text{ kg/m}^3$  at 20 °C. The empty mass of these bottles is around another 12.5 kg, but a new stainless-steel design has almost half empty mass. The new aluminium bottle holds 6 kg (13 kg total, 290 mm diameter and 376 mm height). For high power or cold ambient, propane bottles work better.

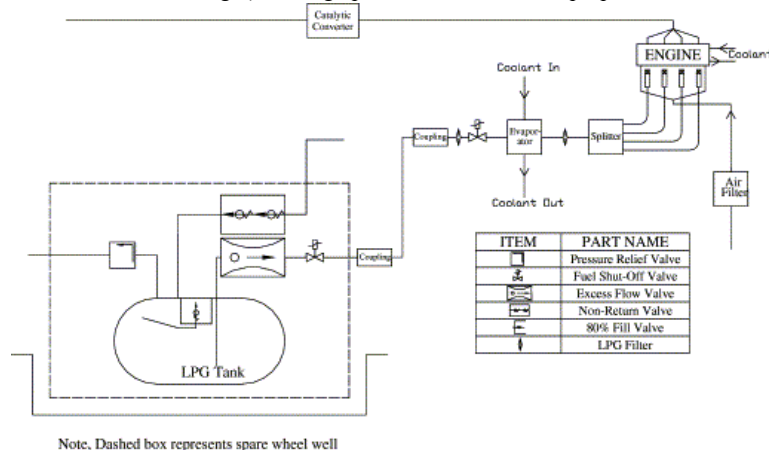


Fig. 3. Fuel installation in a propane vehicle.

LPG is also marketed in small expandable containers for laboratory use (containing some 50..300 g of LPG, 190 g is the commonest), and portable 'camping gas' bottles (containing some 2..4 kg of LPG, 2.8 kg is commonest), with a rough molar composition of 40% propane and 60% butanes (n-butane and iso-butane). For vehicles EN-589-1993 applies.

LPG is transported in large liquefied-containers on ships. Here, an engineering trade-off must be found to minimise transportation costs, since large pressurised containers are expensive to build (thickness,  $\delta$ , must be proportional not only to gauge pressure,  $\Delta p$ , but to diameter,  $D$ , as a force balance on a hemispherical free-body shows:  $\pi D \delta \sigma = (\pi D^2/4) \Delta p$ ,  $\sigma$  being the normal stress in the shell material). Different solutions exist to carry the LPG in liquid state: 1) a heavy pressurized tank at room temperature ( $C_3H_8$  at 50 °C has  $p_v=1.7$  MPa), 2) a strongly refrigerated tank at ambient pressure ( $C_3H_8$  at 110 kPa must be kept at  $-40$  °C; notice that some overpressure, e.g.  $\Delta p=10$  kPa, is necessary to avoid boil-off due to ambient-pressure fluctuations and shell collapse on depression), and 3) any intermediate refrigeration with corresponding pressurization. As for year 2000, there were around 800 LPG ships, some 50% of them with small capacity ( $<10\,000\text{ m}^3$ ) operating at ambient temperature (and  $p<1.8$  MPa), the first one in 1931, of  $1200\text{ m}^3$ , operating at 0.55 MPa; some 40% of medium capacity ( $<30\,000\text{ m}^3$ ) operating at medium pressures, 0.2..0.8 MPa, and medium temperatures,  $-30..10$  °C; and some 10% of large capacity (up to  $100\,000\text{ m}^3$ ) operating at ambient pressures (and  $-50\text{ °C}<T<-30\text{ °C}$ ).

All gaseous fuels are odourless (except those containing traces of  $H_2S$ ), and odour markers (sulfur-containing chemicals as thiols or mercaptans) are introduced for safety.

Table 1. Data for some gaseous fuels.

	NG (Algeria <sup>a</sup> )	NG (North Sea)	Propane (commercial)	Butane (commercial)	Biogas (typical)
$\rho$ at 15 °C [ $kg/m^3$ ] <sup>b</sup>	0.74	0.74	2.0 gas, 520 liquid	2.4 gas, 560 liquid <sup>c</sup>	1.1..1.2
HHV (LHV) [MJ/kg]	54.3 (49)	53 (48)	50 (46)	49 (45)	33 (30)
CH <sub>4</sub> %vol	92	82			60
C <sub>2</sub> H <sub>6</sub> %vol	7	9			
C <sub>3</sub> H <sub>8</sub> %vol	1	5	>80	<30	
C <sub>4</sub> H <sub>10</sub> %vol		2	<20	>70	
olefins %vol			<20	<20	
N <sub>2</sub> %vol		1			2 <sup>d</sup>
CO <sub>2</sub> %vol		1			40

<sup>a</sup>For natural gas delivered through LNG carriers, which follows a different treatment than the one pumped through gasoducts (e.g. methane content may be as low as 83% in the latter case).

<sup>b</sup>Standard conditions are usually defined as 15 °C and 100 kPa, whereas normal conditions are usually defined as 0 °C and 101 kPa, thus one standard cubic metre equals 0.95 normal cubic metres (sometimes written  $1\text{ Sm}^3=0.95\text{ Nm}^3$ ).

<sup>c</sup>Thermal expansion of liquid propane  $\alpha=1.5\cdot 10^{-3}\text{ K}^{-1}$ .

<sup>d</sup>Typical biogas composition: 55..65% CH<sub>4</sub>, 35..45% CO<sub>2</sub>, 1..4% N<sub>2</sub>, 1..2% H<sub>2</sub> and <1% H<sub>2</sub>S and H<sub>2</sub>SO<sub>4</sub> before desulfuration.

## CH<sub>4</sub> and NG

[Basic thermodynamic data](#) can be found aside. [Methane](#) is obtained from [natural gas](#), the major industrial gas. Pure methane is a laboratory stuff for reference purposes; commonly, methane is used to mean natural gas (where typical methane content is 90% by volume).

Natural gas is a flammable gaseous mixture, composed mainly of methane: 75%..98% CH<sub>4</sub>, 1%..13% C<sub>2</sub>H<sub>6</sub>, 0..2% C<sub>3</sub>H<sub>8</sub>, and minor concentrations of H<sub>2</sub>O, CO, CO<sub>2</sub>, N<sub>2</sub>, He, etc. It is found on many underground cavities, either as free deposits (e.g. Indonesia, Algeria, New Zealand) or linked to petroleum fields (e.g. Saudi Arabia, Nigeria), and, although local consumption still dominates (in 2003 only 24% of world production was exported), export share is increasing (e.g. 50% estimation for 2030). Since the mid 20th century it is traded by large continental gasoducts (up to 2 m in diameter, with sensors and control valves every 25 km and pumping stations every 100 km) and LNG-ships (Liquefied Natural Gas ships up to 140 000 m<sup>3</sup> in capacity); in 2003, 73% of NG-exports was by gasoduct, and 27% by LNG carriers. The main producers in EU are Russia (growing), Norway and UK (declining).

LNG-ships were developed in 1960s, the Algeria-Italy submarine-gasoduct started operation in 1983, and the Algeria-Spain one in 1997. Large LNG reservoirs of up to 50 000 m<sup>3</sup> and gasholders of up to 100 000 m<sup>3</sup> are used as accumulators, but underground cavities (natural or artificial) seem a better solution. Before putting the dry natural gas on the market, it is sweetened (H<sub>2</sub>S and CO<sub>2</sub> are removed by amine absorption), dehydrated (by glycol absorption, to avoid water freezing and hydrate formation), and some liquefying fractions are extracted (to produce 'LPG', by isentropic expansion); natural gas associated to oil fields may contain appreciable fractions of butane and heavier hydrocarbons, and it is then called 'wet gas'. Differences in natural gas composition have a sizeable impact on heating value, particularly on volume basis; e.g. HHV=36 MJ/m<sup>3</sup> for NG from Russia, 38 MJ/m<sup>3</sup> for NG from USA, 33 MJ/m<sup>3</sup> for NG from Netherlands, 39 MJ/m<sup>3</sup> for NG from UK, 42 MJ/m<sup>3</sup> for NG from Algeria, etc.

The gasoduct under the Gibraltar Strait consists of two 0.5 m in diameter welded steel pipes (tested at 16 MPa) with a concrete overcoat to protect it from anchors, 50 m apart, with 45 km undersea length up to 400 m deep (the one under Sicily Strait reaches 600 m depth).

## Cl<sub>2</sub>

[Chlorine](#), Cl<sub>2</sub>(g) (Gr. *chloros*: greenish yellow) is a greenish-yellow gas discovered in 1774 by Scheele and named in 1810 by Davy.  $M=0.071$  kg/mol,  $T_m=-102$  °C,  $T_b=-34.4$  °C. It is used to make plastics (PVC), for potable water, paper-pulp bleaching, and as a strong oxidant.

It is produced by the electrolysis of brine,  $2\text{NaCl}(\text{aq})+2\text{H}_2\text{O}(\text{l})=2\text{NaOH}(\text{aq})+\text{H}_2(\text{g})+\text{Cl}_2(\text{g})$ , in a diaphragm cell, which is basically a container separated down the centre with a porous (commonly asbestos) diaphragm. The container has brine (NaCl in water) pumped into the left hand side. Above is a Ti anode where Chlorine is produced, and piped off. Spent brine flows through and at the steel cathode on this side, water is reduced to form H<sub>2</sub> (and OH which forms NaOH with the sodium left over from before). This sodium hydroxide solution is then piped out from the bottom, while the H<sub>2</sub> is piped off the top. The two

gases must be separated because they would react explosively if they came into contact. The diaphragm cell above has replaced a similar one using a flowing mercury cathode due to concerns about mercury poisoning. Also, many problems with chlorine-containing solvents have been found (specifically the ozone layer) which makes this process somewhat less favourable.

The fact that the above cell produces  $\text{Cl}_2$ ,  $\text{H}_2$  and  $\text{NaOH}$  is very convenient, since all three are useful products, and the cell uses comparatively little energy...uses

- Chlorine -- Dry cleaning solvents, refrigerants, PVC, disinfectant
- Hydrogen -- Ammonium production, fuel cells, reducing agent.
- $\text{NaOH}$  -- Neutralizing acids, producing soap, aluminium production

### **HCl**

[Hydrochloric acid](#) is an irritating colourless gas with  $M=0.03646$  kg/mol,  $T_m=-115$  °C,  $T_b=-85$  °C,  $\rho_L=1190$  kg/m<sup>3</sup> at  $T_b$ , and its solubility in water at 0 °C is 0.823 kg HCl / kg H<sub>2</sub>O.

### **He**

[Basic thermodynamic data](#) can be found [aside](#). [Helium](#) is the second most abundant element in the universe (24% of our galaxy mass), but very scarce on Earth (it was first discovered as an unknown yellow spectral line from the Sun corona in a solar eclipse in 1868). In 1882 He was found as a spectral line in of Mount Vesuvius lava. In 1903, a large He source was found in the USA in a non-flammable natural gas drilling (2% He, 72% N<sub>2</sub>, 15% CH<sub>4</sub>, 1% H<sub>2</sub>...). For many years the United States produced over 90% of commercially usable helium in the world (the rest in Canada, Poland and Russia). In the 1990s helium was found in Algeria, which is now the second world's and main EU supplier. The world's first helium-filled airship flew in 1921.

### **H<sub>2</sub>**

[Basic thermodynamic data](#) can be found [aside](#). [Hydrogen](#) was first produced by accident in 1670 by R. Boyle, by reaction of metals and acids; in 1766, Henry Cavendish studied it and called it 'flammable air', and in 1781 Joseph Priestley produced water by igniting hydrogen in oxygen. But it was in 1783 when Lavoisier repeated Cavendish experiments and realized that this was a new gas and name it 'hydrogen'. The gas was so light, that the same year (1783), just after the first manned hot-air [balloon](#) flight, A.C. Charles made the first H<sub>2</sub> balloon (first flight unmanned). H<sub>2</sub> is used in the chemical industry, as a rocket fuel, and in the electronics and food industries. As of year 2000, more than 99% H<sub>2</sub> production ( $6 \cdot 10^9$  kg/yr) is used as a chemical stuff for ammonia, methanol and crude-oil refinery, the rest in electronics, food and metal industries. See [Fuel properties](#) for a review of hydrogen production, storage, use, safety, price, etc.

### **NH<sub>3</sub>**

[Basic thermodynamic data](#) can be found [aside](#). [Ammonia](#) is a colourless, pungent gas composed of nitrogen and hydrogen. It is the simplest stable compound of these elements and serves as a starting material for the production of many commercially important nitrogen compounds. Pure ammonia was

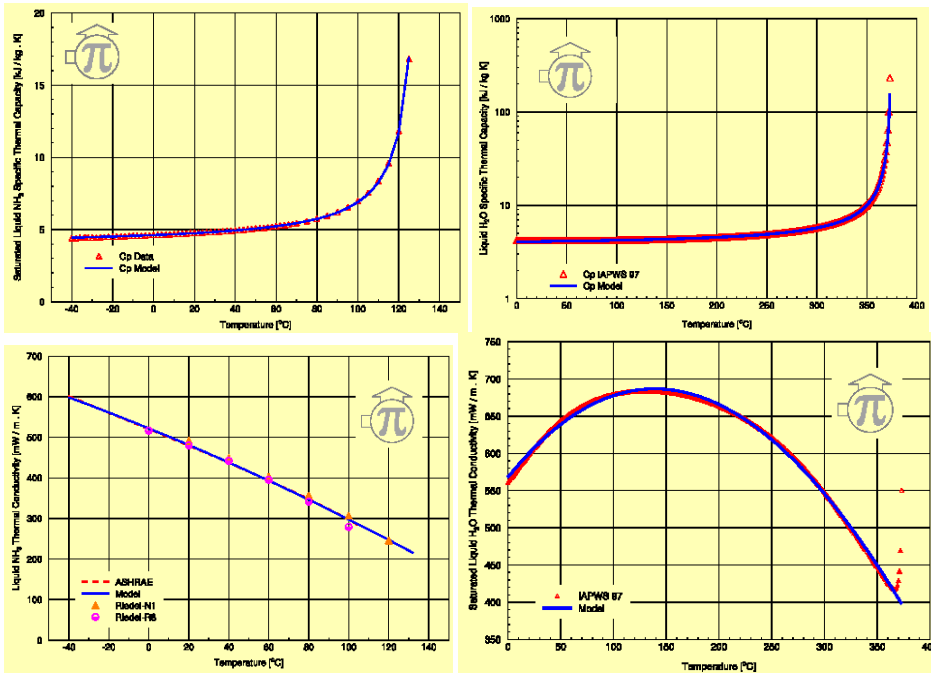
first prepared by Joseph Priestley in 1774, and its exact composition was determined by Claude-Louis Berthollet in 1785.

In classical times (described by Pliny), salt ammoniac was discovered by accident through burning the dung of camels in the temple of Ammon at Siwa oasis in Libya.

Ammonia is highly soluble in water, forming an alkaline solution called ammonium hydroxide. Moreover, it becomes highly reactive when dissolved in water and readily combines with many chemicals. Ammonia is easily liquefied by compression or by cooling to about  $-33^{\circ}\text{C}$

Because ammonia can be decomposed easily to yield hydrogen, it is a convenient portable source of atomic hydrogen for welding.

It can burn in air with air/fuel ratio  $A=6.05$ .  $T_{\text{autoign}}=650^{\circ}\text{C}$ . LEL-UEL=15.5%..27%.



## SF<sub>6</sub>

[Basic thermodynamic data](#) can be found aside. [Sulfur hexafluoride](#) is a colourless, odourless, non-combustible, dielectric gas with low toxicity, slightly soluble in water. Its main use (80% of world production) is as a dielectric gaseous insulator for electrical equipment such as transformers, circuit breakers, and other electrical switchgear, having a breakdown strength about 3 times that of air. It has

good heat transfer properties and very effective absorber of IR energy (i.e. high GWP=3600). Above 500 °C it decomposes to fluorine, reacting with just about anything, especially any water vapour.

Dielectric constant,  $\epsilon$ , is the square of the refractive index,  $n$ , that for non-polar dielectric gases are related to gas density,  $\rho$ , by the Lorentz-Lorenz formula (named after the Danish mathematician and scientist Ludwig Valentine Lorenz, who published it in 1869, and the Dutch physicist Hendrik Lorentz, who discovered it independently in 1870.), also known as the Clausius-Mossotti equation:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{n^2 - 1}{n^2 + 2} = Q\rho = \frac{\alpha N_A}{3} \rho$$

where  $Q$  is known as refractivity or Lorentz-Lorenz coefficient,  $\alpha$  the electronic polarizability and  $N_A$  Avogadro's number.  $Q=77 \cdot 10^{-6} \text{ m}^3/\text{kg}$  for SF<sub>6</sub>.

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