Industrial Gases Processing

Edited by
Heinz-Wolfgang Häring

Translated by Christine Ahner

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Foreword

Industrial gases have become over a period of more than a century ubiquitous ingredients of our daily activities, e.g. metal fabrication, metallurgy, petrochemicals, food processing, healthcare, and many more.

In 2006, the business generated globally with industrial gases exceeded the 50 billion US dollar volume.

At The Linde Group, generations of scientists and engineers have been working in this field, determining the physical and chemical properties, developing processes for the production, purification and application of industrial gases, as well as their safe handling, storage and transportation.

This book, written and compiled by numerous experts and edited by Dr. Wolfgang Häring, is an authoritative, accurate, and useful single-source reference for those who work in this industry, for students or simply for the users of industrial gases. Details are also offered concerning the historical background of these molecules.

The term "industrial gases" is herewith intended to include also the category of "medical gases", which, while being produced by means of "industrial" processes, have meanwhile become real drugs and are subject to Good Manufacturing Practices.

It is my pleasure to commend the editor as well as the authors of this outstanding piece of technical literature for their relentless and professional quest for precision and completeness, which for sure will be highly appreciated by all readers.

Pullach, October 2007

Dr. Aldo Belloni
Linde AG

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1
Introduction

The history of industrial gases is inextricably linked to the rapid pace of industrialisation that marked the nineteenth century. The large-scale generation of certain gases opened the door for new types of technologies and production processes.

Acetylene, for example, was discovered by *E. Davy* in 1836. A significant landmark followed in 1862, when *F. Wöhler* succeeded in producing acetylene from the reaction between calcium carbide and water. Then, in 1892, *T. L. Wilson* and *H. Moissan* discovered a process for generating calcium carbide in an electric furnace. This paved the way for industrial-scale production of acetylene in 1895 (see also Section 8.2). Initially, acetylene was mainly used for lighting purposes due to its bright flame. Later, its high combustion temperature in oxygen prompted development of autogenous cutting and welding technology, starting in 1901.

An even more important step from today's perspective was the liquefaction of air by *Carl von Linde,* marking the birth of an entirely new industry. *C. v. Linde* employed the Joule–Thomson effect, decreasing the temperature of the gas by adiabatic expansion. In 1895, he achieved continuous generation of liquid air at a yield of three litres per hour using a laboratory plant [1.1]. The following years saw the construction and delivery of the first small commercial air liquefaction plants. Figure 1.1 shows a typical early air liquefier (ca. 1899).

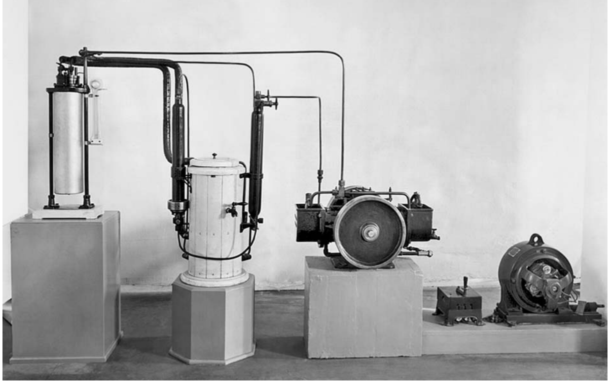

Fig. 1.1 Typical assembly of a Linde air liquefier (ca. 1899).

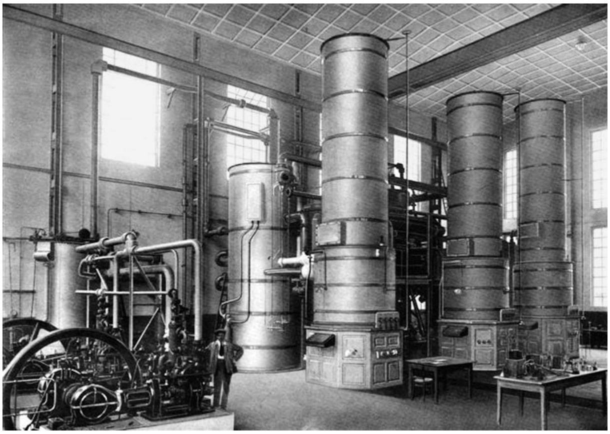

Fig. 1.2 Linde air separation unit for simultaneous production of 200 $m^3 h^{-1}$ oxygen and 1,800 $m^3 h^{-1}$ nitrogen (ca. 1919).

In 1902, *C. v. Linde* started using a rectification process to separate liquid air for continuous oxygen production at a purity above 99%. High-purity nitrogen was first recovered in 1905. And five years later, in 1910, simultaneous production of oxygen and nitrogen became possible with *C. v. Linde's* invention of the double-column rectifier. Figure 1.2 shows one of these plants (ca. 1919).

During this period, there was particularly strong competition between *C. v. Linde* and *G. Claude*, one of the founders of L'Air Liquide S.A in 1902, thus spurring further development of air separation technology and resulting in important improvements [1.2].

A century on, innovations in air separation technology have spawned some impressively large plants: Air Liquide installed an air separation unit in 2004 to feed pressurised gaseous oxygen (GOX) to a Sasol partial oxidation plant in South Africa at a rate of 3,500 td^{-1}, for instance. In 2006, Linde received a construction order from Shell for the biggest air separation facility ever built, with eight units producing a total of 30,000 td^{-1} GOX to feed Pearl, the world's largest gas-to-liquid (GTL) plant in Qatar. And since 2000, the four units of the Linde air separation facility at Cantarell, Mexico have been producing a total of 40,000 td^{-1} pressurised gaseous nitrogen (GAN), which is injected into the well to enhance oil recovery (see Figure 1.3). A fifth unit is now also in operation.

The industrial-scale availability of nitrogen and hydrogen at the turn of the 19th to the 20th century enabled a host of new applications. The BASF company, for example, succeeded in developing an ammonia synthesis from nitrogen and hydrogen in 1913. This paved the way for mass production of fertilisers.

A good overview of the historical development and pioneers of industrial gases may be found in [1.3–1.5].

Fig. 1.3 Air separation unit at Cantarell, Mexico (2000).

The following table sets out some of the chronological milestones in the history of industrial gases:

1766	Production of pure hydrogen by *H. Cavendish*
1783	First flight of a hydrogen-filled balloon (*J. Charles*) using hydrogen generated from the reaction between iron and sulphuric acid
1853	*J. P. Joule* and *W. Thomson* observe a temperature decrease caused by the adiabatic expansion of compressed gases (Joule–Thomson effect)
1868	First operation under nitrous oxide ("laughing gas")/oxygen anaesthetic performed by *Andrews*
1892	*H. Moissan* and *Th. L. Wilson* discover a method for generating calcium carbide in an electric furnace, enabling industrial production of acetylene in 1895
1895	*C. v. Linde* builds the first technical apparatus for the liquefaction of air
1898	Liquefaction of hydrogen by *J. Dewar*
1898	Discovery of the noble gases neon (Ne), krypton (Kr) and xenon (Xe) (1868: helium, He, 1894: argon, Ar)
1900	First flight of a hydrogen-filled Zeppelin airship
1901 onwards	The high combustion temperature of acetylene in oxygen inspires development of autogenous welding technology
1902	*C. v. Linde* employs a rectification process for technical production of liquid oxygen
1902	*G. Claude* invents the piston expansion machine for air liquefaction
1908	Liquefaction of helium by *H. Kamerlingh-Onnes*

1910	*C. v. Linde* invents the double-column rectifier for simultaneous production of oxygen and nitrogen
1913	Technical ammonia synthesis from nitrogen and hydrogen by *F. Haber* and *C. Bosch* (BASF)
1917	First extraction of helium from natural gas in Hamilton, Canada
1922	Technical methanol synthesis from synthesis gas by *G. Patart* (BASF)
1925	Development of Fischer–Tropsch synthesis, i.e. catalytic synthesis of hydrocarbons using synthesis gas (mixture of hydrogen and carbon monoxide) by *F. Fischer* and *H. Tropsch*. Industrial application since 1932
1936 onwards	Commercial use of the Lurgi process to generate synthesis gas from carbon using oxygen and steam
1940s onwards	Use of Ar and He in tungsten inert gas (TIG) welding
1942	Use of liquid oxygen for a V2 missile
1950s onwards	Use of carbon dioxide in metal active gas (MAG) welding
1960s onwards	Use of high-purity electronic gases in manufacturing semiconductor elements (contaminations in lower ppb range)
1961	First continuous helium/neon laser
1961	Linz-Donawitz (LD) process for steel manufacture by injecting oxygen into the converter
1962	First use of liquid nitrogen for cryogenic (shock) freezing of food
1963	Use of liquid hydrogen and liquid oxygen as fuel for space travel (USA)
1965	Commercial use of argon-oxygen decarburization (AOD) process to produce austenitic stainless steel
1980s onwards	Use of liquid helium for superconducting magnets in nuclear magnetic resonance tomography, for particle accelerators and fusion reactors
1980s onwards	CO_2 laser for cutting metal
1999	First public hydrogen fuelling station for cars and buses at Munich Airport, Germany

Which gases are classified as industrial today? According to [1.6], the term “industrial gases” is “a collective term for combustible and non-combustible gases generated on an industrial scale, such as hydrogen, oxygen, nitrogen, carbon dioxide, acetylene, ethylene, noble gases, ammonia, water gas, generator gas, city gas, synthesis gas, etc.”. Taking global market share (percentage of sales), [1.9] identifies the major candidates here as oxygen (29%), nitrogen (17%), argon (10%), carbon dioxide (9%), acetylene (7%), hydrogen (5%) and helium (1%). The total share of all other industrial gases together is 22% of the global gas market. This includes carbon monoxide, nitrous oxide (“laughing gas”), the noble gases krypton, xenon and neon, and a large number of specialty gases and gas mixtures for different applications. Some of the most common specialty gases here are nitrogen trifluoride, silane, arsine, phosphane (phosphine), tungsten hexafluoride and sulphur hexafluoride (see Chapter 9).

Who are the main suppliers? Companies that supply industrial gases can be divided into two tiers according to sales. Three different supply models are used – on-site (including pipeline), bulk and cylinder delivery.

In the first tier, with sales exceeding USD 1 billion, there are seven major companies whose combined gas-related revenue accounted for over 75% of the global market at the end of 2005:

AL:	Air Liquide (French gas company)
BOC:	BOC Gases (UK gas company)
AP:	Air Products and Chemicals, Inc. (US gas company)
Praxair:	Praxair, Inc. (US gas company)
Linde:	Linde Gas (German gas company)
TNS:	Taiyo Nippon Sanso Co. (Japanese gas company)
Airgas:	Airgas, Inc. (major US distributor)

Figure 1.4 [1.7] shows the global market shares of the first-tier companies in 2005. This reflects the market situation prior to the acquisition of the BOC Group by Linde AG to form a leading gas and engineering company under the name of The Linde Group in 2006.

The second tier, with sales below USD 1 billion, contains a larger number of companies such as Iwatani (Japan), Messer (Germany), Air Water (Japan), Sapio (Italy), Cryoinfra (Mexico) and Indura (South America).

In addition, there are numerous smaller gas companies active at national or even regional levels. The strength of local gas companies often lies in the high costs entailed in transporting compressed gas in steel cylinders and cryogenically liquefied gas in tank trucks. Production in the customers' vicinity is therefore a more economical alternative.

The value of the global industrial gas business reached USD 49 billion (EUR 39 billion) in 2005, an increase of 9% from 2004. Indeed, for the seven first-tier

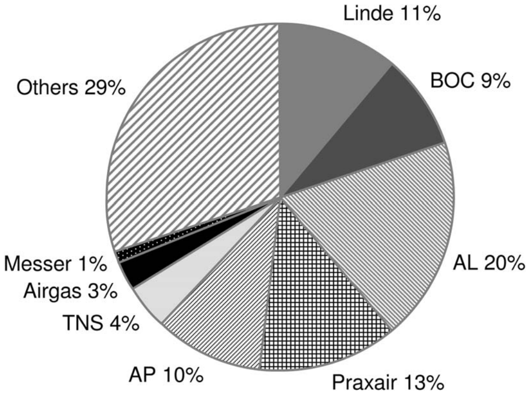

Fig. 1.4 Global market shares of industrial gas companies, 2005.

Industry	**Gas Market Value ($M)**	**Share %**	**Growth Forecast CAGR %**
Chemicals	9 443	19 %	9.1
Metallurgy	6 831	14 %	8.6
Food	3 373	7 %	5.2
Manufacturing	14 543	30 %	7.8
Electronics	6 407	13 %	9.7
Pulp & Paper	513	1 %	4.3
Healthcare	3 332	7 %	7.4
Glass	880	2 %	6.2
Other	3 314	7 %	4.2
Global Total	**48 637**	**100 %**	**7.8**

Fig. 1.5 Global gas business by end-use sector, 2005.

companies, the increase was as high as 12.1% [1.7]. The leading markets are still North America (33%) and Western Europe (29%), which remain far ahead of the rest of the world. The forecast for 2005 to 2010 anticipates a compound annual growth rate of 7.8% for the industrial gas business, with the highest rates expected in the Middle East, Eastern Europe and Asia [1.7] (see also [1.8]).

Finally, who are the end-users? The applications of industrial gases span medicine, food, metallurgy, glass, ceramics and other minerals, rubbers and plastics, paints, environmental protection, water treatment, chemicals, cutting and welding, safety, semiconductors and aerospace, to name just a few. Figure 1.5 provides an overview of the main industries and market sectors supplied by gas companies, together with a growth forecast for 2005 to 2010 [1.7] (see also [1.9]). The chemical, healthcare and electronics industries are set to be the main growth drivers.

Various associations have been set up to cater for the common interests of industrial gas companies worldwide. These span all fields of activity from gas production through storage, transport and delivery to the actual application, not forgetting equipment manufacture [1.10]. Two of the main associations are

- the Compressed Gas Association (CGA) and
- the European Industrial Gases Association (EIGA)

The North-American CGA [1.11] was established as far back as 1913. Its European counterpart is the EIGA [1.12]. The EIGA was preceded by the “Commission Permanente Internationale (CPI) de l’acétylène, de la soudure autogène et des industries qui s’y rattachent”, founded in Paris in 1923, which merged with the EDIA, the European Dry Ice Association in 1989, maintaining the name CPI. The institution started operating as the European Industrial Gases Association (EIGA) in 1990 and is currently headquartered in Brussels.

These associations were founded with a view to self-regulation and to enable joint solutions to safety issues. Right from the beginning, the main task of the associations was to define and introduce safety standards and implement regulations. This was in response to various accidents – some serious – that occurred in the early days of industrial gas production, involving oxygen and combustible gases such as hydrogen and acetylene. Even now, safety issues still constitute an essential part of the work of these associations. The CGA, EIGA and JIGA, the Japanese Industrial Gas Association, are in particularly close collaboration. Efforts are currently underway to harmonise safety standards worldwide, defining common standards over and above those of individual associations. These safety recommendations are primarily based on the analysis of accidents reported to the association by the companies involved. CGA's goal is to adapt existing standards every five years to reflect the latest knowledge. Section 2.3 also contains information about the safety requirements of air separation plants.

Apart from those mentioned above, there are a number of other industrial gas associations [1.10], including

- China Industrial Gases Industry Association (CIGIA)
- International Oxygen Manufacturers Association (IOMA)
- Asia Industrial Gases Association (AIGA)
- Gases and Welding Distributors Association (GAWDA)

Almost all German companies producing, filling or selling industrial gases are members of the German association Industriegaseverband e.V. (IGV). The IGV [1.13] is a member of the EIGA through its membership of the chemical industry trade association, Verband der Chemischen Industrie e.V. (VCI).

This book focuses on the industrial gases of greatest commercial importance. It describes their history and properties, the processes involved in generating or separating them and their industrial and consumer applications, as well as their distribution logistics. It also discusses the future of hydrogen technology.

At the end of each gas type chapter, the typical gas applications are listed. For reasons of clarity they are divided into industry segments (e.g. metallurgy, chemistry).

The most important applications are described in more detail in concrete application examples. These are indicated in the text by capital letters in bold type (e.g. Example A).

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2
The Air Gases Nitrogen, Oxygen and Argon

2.1
History, Occurrence and Properties

2.1.1
Nitrogen

2.1.1.1 History

Owing to its inertness, nitrogen as an element was discovered relatively late. Still in the 17th century, air was supposed to be a homogeneous substance. Only in the year 1770, *Scheele* and *Priestley* discovered nitrogen (dinitrogen, N_2) as a component of air that does not feed combustion. The chemical symbol N derives from the Latin word "nitrogenium" (nitrum generating). In 1784, *Cavendish* obtained nitrogen oxides and nitric acid through electric discharge in the air. Only at the beginning of the 20th century, atmospheric nitrogen was used for the large-scale production of calcium nitrate (*Frank* and *Caro*, 1902), nitric acid (*Birkeland* and *Eyde*, 1905) and ammonia (*Haber* and *Bosch*, 1913). One prerequisite was the large-scale availability of N_2 through the rectification of liquefied air, successfully performed by *Carl von Linde* as of 1902. N_2 was liquefied by *Cailletet* for the first time in the year 1877. Today about 85% of the N_2-output are used for the production of fertilizers for farming, e.g. ammonia salts, nitrates, lime nitrogen (calcium cyanamide, $CaCN_2$), lime ammonium nitrate and urea [2.1].

2.1.1.2 Occurrence

The content of nitrogen in the upper 16 km thick earth's crust is assessed at a mass fraction of about 0.03%. Thus, it belongs to the more frequently found elements. The atmosphere with a N_2-content of 78.1% volume fraction or 75.51% mass fraction contains the largest quantities with $3.9 \cdot 10^{15}$ t [2.2]. Smaller quantities of N_2 are found dissolved in gases of springs and rock inclusions. Bound nitrogen occurs, for example, in nitrates and ammonium compounds. So since 1825, natural Chile saltpetre mainly consisting of sodium nitrate, has been exploited on a large scale as fertilizer. Today however, this happens mostly to recover the iodine contained within. Bound nitrogen, too, exists in the proteins in all organisms and is returned into the N_2-cycle through decomposition reactions. Nitrogen oxides are formed by the reaction of the airborne oxygen and nitrogen in flashes of lightning, subsequently washed out by rain and deposited on the soil as nitrates (about 0.1 g of nitrate-nitrogen on 1 m^2 of soil in one year).

2.1.1.3 Physical and Chemical Properties

At atmospheric pressure and room temperature, nitrogen is a colourless, odourless and non-flammable gas. At 0 °C and 1.013 bar, 1 L of nitrogen weighs 1.2505 g. N_2 condenses at –195.8 °C to a colourless liquid with a density of 0.812 kg L^{-1} that gets solid at –209.86 °C in the form of white crystals. The solubility of N_2 in water amounts to 23.2 mL per kilogram of water at 0 °C and 1 bar, at 25 °C it is only 13.8 mL kg^{-1}. Consequently, N_2 is less soluble in water than O_2.

The inversion temperature of N_2 is 850 K. Inversion temperature is the temperature below which a gas cools down by adiabatic expansion (Joule-Thomson-Effect). Therefore, N_2 can be liquefied from room temperature by means of counter-cooling of previously expanded cold gas, in contrast to H_2 und He.

Nitrogen is an element of the 5th main group of the periodic system and occurs in compounds in the oxidation stages –3 (e.g. NH_3) to +5 (e.g. HNO_3). In the N_2-molecule, both atoms are linked with a homopolar triple bond which is the reason for the stability and the inert character of the molecule. Therefore, high activation energy has to be supplied for the reaction of N_2 with other substances, e.g. through electric discharge or high temperature. Even at 3000 °C, there is no noticeable dissociation into the atoms ($K = c^2(\mathrm{N}) / c(\mathrm{N}_2) \approx 10^{-6}$). Nitrogen as molecule only reacts with lithium at room temperature and with calcium and magnesium at higher temperatures to the respective metal nitrides. Other metals, such as Al, Ti, V and Cr form nitrides only at red heat. An important product from the reaction with boron is boric nitride which is used as grinding material. Owing to its inert character, N_2 is often used as shielding gas, e.g. in chip production.

The nitrogen atom in compounds is often threefold coordinated and has a tetragonal structure with the free electron pair in one corner of the tetrahedron. Nitrogen occurs in varied forms in organic molecules, e.g. in amines ($R{-}NH_2$), amides ($R{-}C({=}O){-}NH_2$), nitriles ($R{-}C{\equiv}N$), oximes ($R_2C{=}N{-}OH$) and nitrogen-heterocycles (e.g. pyridine) [2.3].

One of the research aims of the past years was the nitrogen fixation under mild conditions, especially from the aspect of the synthesis of plant-based protein through transformation of atmospheric nitrogen into ammonium ions by microorganisms (atmospheric fertilization). This biological nitrogen fixation is catalyzed by the enzyme nitrogenase [2.4]. In addition to that, there are numerous attempts to carry out nitrogen-fixation by chemical means. However, in contrast to the Haber-Bosch-Synthesis of ammonia which requires high pressures and temperatures (475–600 °C, 200 bar), the N_2-fixation should occur under mild conditions. Today, coordination compounds of nitrogen with molybdenum, chrome, rhenium, tungsten, cobalt, nickel, titanium, manganese and all platinum-group metals are known.

2.1.2
Oxygen

2.1.2.1 History

Both *Scheele* (1772) and *Priestley* (1774) discovered oxygen quite independently of each other. *Scheele* collected the developing gas of the thermal decomposition of potassium nitrate and mercury oxide as O_2 (dioxygen), whereas *Priestley* generated oxygen and mercury from heated mercury oxide and demonstrated that at low temperature, this reaction is running reverse to the metal oxide again. The Latin name “oxygenium” (= acid generator) is said to come from the French chemist *Lavoisier* who assumed that oxygen is contained in each acid and determines decisively its properties. *Lavoisier* was the first to recognize combustion as combination of oxygen with a fuel gas.

2.1.2.2 Occurrence

Oxygen is the most frequent element in our living space (atmosphere, hydrosphere and earth’s crust). The weight proportion of oxygen in the upper 16 km of the earth’s crust is assessed at 48.9%; oxygen occurs mainly in the form of compounds. The earth’s atmosphere contains an average of 20.95% of O_2 (23.1% mass fraction), altogether about 10^{15} t. Up to a height of 90 km, the oxygen content of the air is almost constant. At larger heights, O_2 and N_2-molecules are split into atoms due to the ultraviolet portion of the sunlight. The concentration of the atmospheric oxygen is in dynamic balance: Respiration and weathering consume oxygen while oxygen is produced through assimilation (photo synthesis).Via photo synthesis, glucose is generated from CO_2 and H_2O with the help of sunlight simultaneously releasing O_2. About $2.7 \cdot 10^{11}$ t of O_2 arise annually by photo synthesis. Apart from this, oxygen results from the decomposition of water vapour in a height of 70–80 km and from the decay of CO_2 in a height of approx. 115 km, however in considerably smaller quantities. The major oxygen consumer is the sea, with the respiration of sea organisms and the oxidation of organic material as the biggest consumers [2.5].

2.1.2.3 Physical and Chemical Properties

At atmospheric pressure and room temperature, oxygen is a colourless and odourless gas. At 0 °C and 1.013 bar, 1 L of oxygen weighs 1.429 g. O_2 condenses at –182.96 °C to a light-blue liquid with a density of 1.141 kg L^{-1} that solidifies at –218.78 °C in the form of light-blue crystals. The solubility of O_2 in water is 49.1 mL O_2 per litre at 0 °C and 1 bar, dropping to 31.1 mL at 20 °C [2.6]. The inversion temperature of O_2 is 767 °C. The average relative atomic mass is 15.9994. O_2 is paramagnetic in gaseous, liquid and solid state.

Oxygen is an element of the 6th main group (chalcogens) of the periodic table of elements occurring in compounds mainly in the oxidation stage –2 (e.g. H_2O). Besides the biatomic form, even a triatomic form of the elementary oxygen occurs under natural conditions, i.e. ozone (O_3). Between –160 and –196 °C, O_2 dimerizes to unstable $(O_2)_2$-aggregates. With the supply of ignition energy, molecular oxygen turns into an extremely reactive gas, which, under energy release, reacts with a number of substances (e.g. carbon, hydrogen, hydrocarbons, sulphur, phosphorus, magnesium, iron powder) to the corresponding oxides. These oxidation reactions often happen under fire and are described as combustion. The reactions in pure oxygen proceed much more oxidizing and are considerably more intensive than in air (atmospheric oxygen) where O_2 is diluted with N_2 in a ratio of approx. 1 : 4.

Therefore, in plants with O_2-concentrations above 21 vol.%, a series of safety guidelines have to be obeyed (e.g. IGC Doc 13/02, Oxygen Pipeline Systems,) that lay down, for instance, the range of materials and the pressure depending maximum gas velocities for piping in oxygen service. The oxidation effect of O_2 is utilized in steel production by blowing the oxygen into molten steel which reduces the C-content in unalloyed steel from initially 4% to $\ll$ 2% (oxygen refining). In addition, manganese, silicon and phosphorus, also contained in pig iron, are combusted as well and removed as slag from the top. With the temperature ranging under the ignition temperature, oxidation often occurs very slowly, for instance, during rusting of iron and rotting of wood. The reason is the stability of the double bond in the O_2-molecule (binding energy –490.7 kJ mol^{-1}). In the paramagnetic normal state of the molecule (triplet state) two electrons are arranged in two antibonding π^*-orbitals according molecular orbital theory [2.7]. With this biradical structure, dehydrogenation reactions proceeding over an intermediate peroxide radical (R–O–O•) are easily explained. The diamagnetic singlet oxygen (two electrons with antiparallel spin are in an antibonding π^*-molecule orbital) formed photochemically is an effective oxidizing agent and in contrast to triplet oxygen, it adds to many organic double bond systems via [2+2] and [2+4] cycloaddition reactions. Thus, selective oxidations can be carried out on a ton scale in the odorant industry. O_2 forms complexes with a lot of metals, the most important of them is haemoglobin (iron complex), responsible for the oxygen transport in blood due to the reversible O_2 uptake.

2.1.3
Argon

2.1.3.1 History

In 1894, argon (Ar) was discovered by *W. Ramsay* and Lord *John William Rayleigh*, who noticed that “nitrogen” isolated from the air had a higher density (1.2567 g L^{-1} under normal conditions) than nitrogen recovered from ammonia nitrite (1.2505 g L^{-1}). Therefore, apart from nitrogen, they derived the presence of another inert gas in the atmospheric air which is heavier than nitrogen. However, the first to isolate argon was *Cavendish* 100 years before, who obtained a not further reducible gas bubble of 1/120 of the original volume after the removal of O_2 and N_2 from an air volume. Due to its inert chemical behaviour, the gas was named argon (argos = Greek for inert). In the year 1938, fluorescent tubes filled with argon were more and more used in the lighting industry. However, only its application as shielding gas, e.g. for welding purposes, triggered off a high worldwide demand for argon after 1950.

2.1.3.2 Occurrence

Argon is the most frequent noble gas by far. Air contains an average volume fraction of 0.93%. Furthermore water springs in larger depth (Geysire) contain plenty of solved argon. According to the state of the art, argon is obtained by cryogenic air separation.

2.1.3.3 Physical and Chemical Properties

At atmospheric pressure and room temperature, argon is a colourless, odourless and non-flammable gas. At 20 °C and 1.013 bar, 1 L of Ar weighs 1.664 g. Argon condenses at –185.88 °C to a colourless liquid with a density of 1.40 kg L^{-1} and solidifies at –189.2 °C. Thus, the boiling point of argon ranges between that of N_2 and O_2. At 0 °C and 1 bar, the solubility of Ar is 51.5 mL per litre of water. Argon has an average atomic mass of 39.948 and is diamagnetic in gaseous, liquid and solid state.

Argon is a noble gas and thus appears in the 8th main group of the periodic system. This monoatomic gas is completely inert and therefore technically used as shielding gas against oxidation, e.g. in welding. In discharge tubes together with other noble gases, certain colour effects can be obtained.

Attempts to generate real argon compounds such as ArF_2 respect. ArF^+ have failed [2.9]. Together with water, argon forms a hydrate with a dissociation pressure of 106 bar at 0 °C. At 0 °C and above 106 bar, this hydrate is stable. Moreover, with hydroquinone an inclusion compound is known (clathrates) however containing no real chemical bonds [2.8].

2.2
Recovery of Nitrogen, Oxygen and Argon

2.2.1
Introduction

Nitrogen, oxygen and argon are almost exclusively recovered from atmospheric air. Table 2.1 shows the concentration of these gases as well as of further components relevant for air separation. Three separation methods are predominant, namely membrane separation, pressure swing adsorption and low-temperature rectification. These methods will be described in the following. As the cryogenic rectification has a share of far more than 90% on the worldwide production, it will be presented in greater detail. A typical cryogenic process for the recovery of compressed oxygen, nitrogen and argon will be introduced. This process will be used to classify the essential process steps, to characterize the key components and to show how the development of these components has also evolved the processes. Subsequent sections on nitrogen generators, high-purity plants and liquefiers will give an impression of the creativity, by which the cryogenic separation technology has been adapted to meet even special demands of the market.

Table 2.1 Composition of the dry atmosphere.

Volume fraction in the air			
N_2	78.12%	Kr	1.138 ppm
O_2	20.95%	Xe	0.086 ppm
Ar	0.932%	Ne	18 ppm
CO_2	~ 400 ppm	He	5.2 ppm
CO	~ 0.1 ppm	H_2	0.5 ppm
N_2O	0.31 ppm		

2.2.2
Application Range of Membrane Separation, Pressure Swing Adsorption and Cryogenic Rectification

The three separation techniques have different process properties, investment and operating costs. A dedicated segment can be defined for each method, in which it allows for the most economic gas production. Table 2.2 characterizes these segments by their production capacity and gas purity. Of course, the numbers given therein are no sharp limits but indicate reasonable application ranges.

Table 2.2 Application range of membrane separation, pressure swing adsorption and cryogenic rectification.

Gas	Capacity ($m_N^3\ h^{-1}$)	Typical purities	Preferred separation method	Load range
N_2	1–1000	< 99.5% [1]	Membrane	30–100%
	5–5000	< 99.99% [1]	Pressure swing adsorption	30–100%
	200–400 000	any with residual concentrations down to ppb range	Cryogenic rectification	60–100%
O_2	100–5000	< 95%	Vacuum pressure swing adsorption	30–100%
	1000–150 000	any with residual concentrations down to ppb range O_2 content mostly > 95%	Cryogenic rectification	60–100%
Ar			Cryogenic rectification	

[1] Including argon.