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).

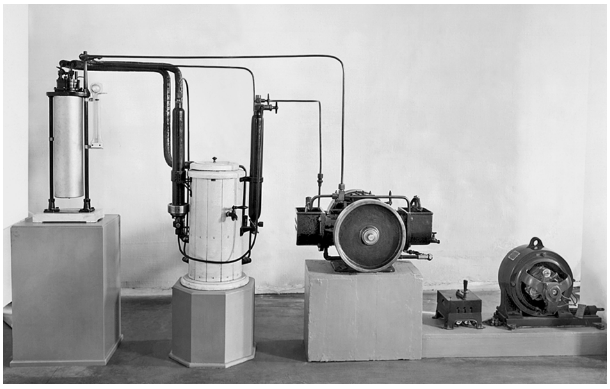

Fig. 1.1 Typical assembly of a Linde air liquefier (ca. 1899).

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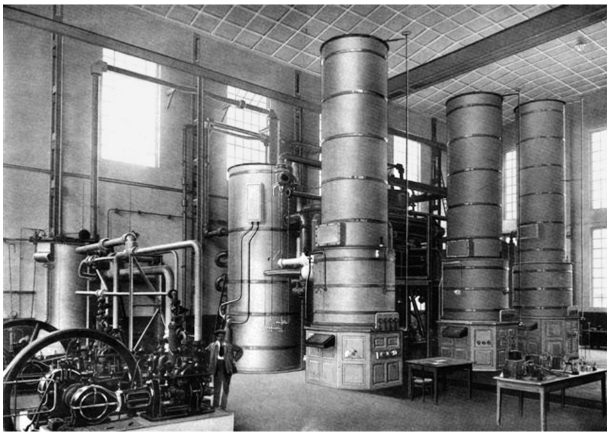

Fig. 1.2 Linde air separation unit for simultaneous production of 200 $m^3 h^{-1}$ oxygen and 1,800 $m^3 h^{-1}$ nitrogen (ca. 1919).

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

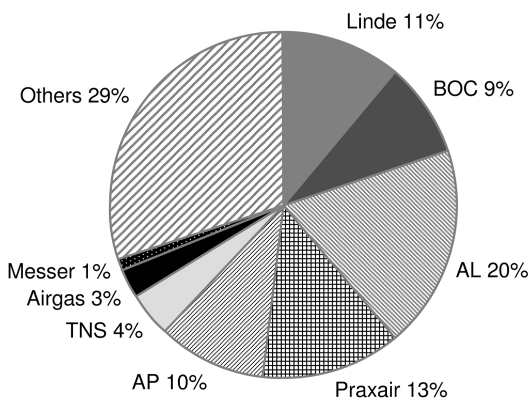

Fig. 1.4 Global market shares of industrial gas companies, 2005.

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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