

Industrial Gases Processing

Edited by
Heinz-Wolfgang Häring

Translated by Christine Ahner



WILEY-VCH Verlag GmbH & Co. KGaA

Industrial Gases Processing

Edited by

Heinz-Wolfgang Häring

Further Reading

A. Züttel, A. Borgschulte, L. Schlapbach (Eds.)

Hydrogen as a Future Energy Carrier

2008

ISBN 978-3-527-30817-0

G. A. Olah, A. Goepfert, G. K. S. Prakash

Beyond Oil and Gas: The Methanol Economy

2006

ISBN 978-3-527-31275-7

Industrial Gases Processing

Edited by
Heinz-Wolfgang Häring

Translated by Christine Ahner



WILEY-VCH Verlag GmbH & Co. KGaA

The Editor

Dr. Heinz-Wolfgang Häring

Lommelstrasse 6
81479 München
Germany

Cover Illustration:

Hydrogen plant, Oberhausen, Germany,
with kind permission of Linde AG

All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Printed in the Federal Republic of Germany
Printed on acid-free paper

Composition Manuela Treindl, Laaber

Printing betz-druck GmbH, Darmstadt

Bookbinding Litges & Dopf GmbH, Heppenheim

ISBN 978-3-527-31685-4

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

Contents

Foreword	<i>V</i>
List of Contributors	<i>XIII</i>
1 Introduction	<i>1</i>
<i>References</i>	<i>7</i>
2 The Air Gases Nitrogen, Oxygen and Argon	<i>9</i>
2.1 History, Occurrence and Properties	<i>9</i>
2.1.1 Nitrogen	<i>9</i>
2.1.1.1 History	<i>9</i>
2.1.1.2 Occurrence	<i>9</i>
2.1.1.3 Physical and Chemical Properties	<i>10</i>
2.1.2 Oxygen	<i>11</i>
2.1.2.1 History	<i>11</i>
2.1.2.2 Occurrence	<i>11</i>
2.1.2.3 Physical and Chemical Properties	<i>11</i>
2.1.3 Argon	<i>12</i>
2.1.3.1 History	<i>12</i>
2.1.3.2 Occurrence	<i>13</i>
2.1.3.3 Physical and Chemical Properties	<i>13</i>
2.2 Recovery of Nitrogen, Oxygen and Argon	<i>13</i>
2.2.1 Introduction	<i>13</i>
2.2.2 Application Range of Membrane Separation, Pressure Swing Adsorption and Cryogenic Rectification	<i>14</i>
2.2.3 Nitrogen Recovery with Membranes	<i>16</i>
2.2.3.1 Physical Principle	<i>16</i>
2.2.3.2 Membrane Technology	<i>16</i>
2.2.3.3 Design	<i>17</i>
2.2.4 Nitrogen and Oxygen Recovery by Means of Pressure Swing Adsorption	<i>18</i>
2.2.4.1 Physical Principle	<i>18</i>

2.2.4.2	Properties of Molecular Sieves	18
2.2.4.3	Nitrogen Recovery	19
2.2.4.4	Oxygen Recovery	20
2.2.5	Cryogenic Rectification	20
2.2.5.1	Process with Air Booster and Medium-Pressure Turbine for the Recovery of Compressed Oxygen, Nitrogen and Argon	21
2.2.5.2	Internal Compression	32
2.2.5.3	Nitrogen Generators	36
2.2.5.4	Liquefiers	37
2.2.5.5	High-purity Plants	38
2.2.5.6	Apparatus	42
2.2.5.7	Design, Assembly and Transport of the Coldbox	57
2.3	Safety Aspects	59
2.3.1	Introduction	59
2.3.3	Air Pollution	61
2.3.4	Ignition in Reboilers	63
2.3.5	Other Hazards in Air Separation Units	64
2.4	Process Analysis Air Separation Units	64
2.5	Applications of the Air Gases	67
2.5.1	Applications of Nitrogen	67
2.5.1.1	Applications of Nitrogen for Inerting and Purging	67
2.5.1.2	Applications of Nitrogen for Cooling, Preserving and Deep-Freezing	74
2.5.2	Applications of Oxygen	83
2.5.3	Applications of Argon	104
	<i>References</i>	108
3	The Noble Gases Neon, Krypton and Xenon	111
3.1	History and Occurrence	111
3.2	Physical and Chemical Properties	111
3.3	Recovery of Krypton and Xenon	112
3.3.1	Pre-enrichment in the Air Separator	113
3.3.2	Recovery of Pure Kr and Xe	115
3.3.2.1	Catalytic Combustion of Hydrocarbons	115
3.3.2.2	Cryogenic Separation	116
3.4	Recovery of Neon	118
3.4.1	Pre-enrichment	118
3.4.2	Fine Purification	119
3.5	Industrial Product Purities and Analytics	120
3.6	Applications of the Noble Gases Neon, Krypton and Xenon	121
3.6.1	Applications of Neon	121
3.6.2	Applications of Krypton	121
3.6.3	Applications of Xenon	122
	<i>References</i>	124

4	The Noble Gas Helium	125
4.1	History, Occurrence and Properties	125
4.1.1	History	125
4.1.2	Occurrence	125
4.1.3	Physical and Chemical Properties	127
4.2	Recovery	127
4.3	Applications	131
	<i>References</i>	134
5	Hydrogen and Carbon Monoxide: Synthesis Gases	135
5.1	History, Occurrence and Properties	135
5.1.1	Introduction	135
5.1.2	History of Synthesis Gas	136
5.1.3	Hydrogen	136
5.1.3.1	History and Occurrence	136
5.1.3.2	Physical and Chemical Properties	137
5.1.4	Carbon Monoxide	141
5.1.4.1	History and Occurrence	141
5.1.4.2	Physical and Chemical Properties	141
5.2	Production of Synthesis Gas	143
5.2.1	Production of Hydrogen by Electrolysis	143
5.2.2	Production of Synthesis Gas from Hydrocarbons	144
5.2.2.1	Generation of Synthesis Gas by Steam Reforming	145
5.2.2.2	Synthesis Gas Generation by Partial Oxidation (PO)	146
5.2.2.3	Generation of Synthesis Gas by Autothermal Reforming (ATR)	148
5.2.3	Synthesis Gas Processing	150
5.2.3.1	Water–Gas Shift Reactor	150
5.2.3.2	Removal of Carbon Dioxide and Acid Gases	150
5.2.3.3	Methanation	151
5.2.3.4	Pressure Swing Adsorption (PSA)	151
5.2.3.5	Membrane Processes	152
5.2.3.6	Cryogenic Separation Processes	153
5.2.4	Processes for the Production of Synthesis Gas from Hydrocarbons	156
5.2.4.1	Reformer Plant for the Production of Hydrogen	157
5.2.4.2	Reformer Units for the Generation of CO and H ₂	158
5.2.4.3	PO-plant for the Production of CO and H ₂	159
5.3	Process Analytics	161
5.4	Applications of Hydrogen, Carbon Monoxide and Syngas	164
5.4.1	Applications of Hydrogen	164
5.4.1.1	Hydrogen Use in the Chemical Industry	165
5.4.1.2	Hydrogen as an Energy Carrier	166
5.4.1.3	Fuel Cells	177

5.4.2	Applications of Carbon Monoxide	182
5.4.3	Applications of Synthesis Gas (Mixtures of CO and H ₂)	182
	<i>References</i>	182
6	Carbon Dioxide	185
6.1	History, Occurrence, Properties and Safety	185
6.1.1	History	185
6.1.2	Occurrence	185
6.1.3	Physical and Chemical Properties	186
6.1.4	Safety Issues	188
6.2	Recovery of Carbon Dioxide	189
6.2.1	Sources of Carbon Dioxide Recovery	190
6.2.2	Pre-purification, Enrichment, Extraction, Capture	191
6.2.3	Standard Process for the Liquefaction of Carbon Dioxide	193
6.2.3.1	Compression and Water Separation	194
6.2.3.2	Adsorber Station	194
6.2.3.3	Liquefaction and Stripping of Lighter Components	194
6.2.3.4	Refrigerating Unit	194
6.2.4	Process Steps to Obtain High Product Purity and Recovery Rate	195
6.2.4.1	Scrubbing	196
6.2.4.2	Adsorption and Chemisorption	197
6.2.4.3	Catalytic Combustion	198
6.2.4.4	Improvement of the Carbon Dioxide Recovery Rate	198
6.2.5	Carbon Dioxide Recovery from Flue Gas	198
6.2.6	Production of Dry Ice	200
6.3	Applications	201
	<i>References</i>	215
7	Natural Gas	217
7.1	History	217
7.2	Occurrence	218
7.3	Consumption	220
7.4	Natural Gas Trade	220
7.5	Composition	223
7.6	Process of Natural Gas Treatment	224
7.6.1	Dew-point Adjustment	224
7.6.2	Separation of Liquefied Petroleum Gas	225
7.6.3	Ethane Separation	229
7.6.4	Liquefaction	231
7.6.5	Nitrogen Separation	236
7.7	Applications	238

8	Fuel Gases	239
8.1	Introduction	239
8.2	Acetylene C_2H_2	240
8.2.1	Acetylene and the Beginnings of Welding Engineering	240
8.2.2	Physical Properties	241
8.2.3	Acetylene Decomposition – Deflagration	243
8.2.4	Ignitable Mixtures	243
8.2.5	Liquefaction of Acetylene – Acetylene Hydrate	243
8.2.6	Acetylene Hydrate	244
8.2.7	Acetylides	244
8.2.8	Extraction Processes	246
8.2.8.1	Acetylene Generated via Carbide	246
8.2.8.2	Petrochemically Generated Acetylene	246
8.2.9	Gas Supply	246
8.2.9.1	Storage of Dissolved Acetylene in Cylinders	246
8.2.9.2	Design of a Gas Supply System	247
8.2.10	Autogenous Engineering Applications	247
8.2.11	Regulations	248
8.3	Ethene C_2H_4	249
8.3.1	Physical Properties	249
8.3.2	Production Processes	249
8.3.3	Application and Use	249
8.3.4	Gas Supply and Safety	249
8.3.5	Regulations	251
8.4	Other Fuel Gases	251
8.5	Applications	252
	<i>References</i>	253
9	Specialty Gases	255
9.1	Introduction	255
9.2	Pure Gases	256
9.2.1	Definitions	256
9.2.2	Quality Criteria	256
9.2.3	Sources/Production	257
9.2.4	Purification/Processing	257
9.2.5	Application Examples	258
9.3	Gas Mixtures/Calibration Gas Mixtures	261
9.3.1	Definitions	261
9.3.2	Production [9.9]	263
9.3.2.1	Technical Feasibility	263
9.3.2.2	Pretreatment of Containers	263
9.3.2.3	Preparation Methods	264
9.3.2.4	Analytical Quality Assurance	267
9.3.3	Application Examples	269

9.4	Electronic Gases	269
9.4.1	Definition/Special Demands	269
9.4.2	Application Examples	271
9.5	Disposal	271
9.6	Transfer of Gases	272
9.6.1	Selection of the Materials	272
9.6.2	Physical Interaction Forces	272
9.6.3	Tightness of the Gas Supply System	273
9.6.4	Purging of the Gas Supply System	273
	<i>References</i>	275
10	Gases in Medicine	277
10.1	Introduction	277
10.2	Medicinal Oxygen	278
10.2.1	Home-therapy	278
10.2.2	Hospitals and Other Fields of Application	280
10.3	Gases for Anaesthesia	280
10.3.1	Medical Nitrous Oxide (Laughing Gas)	280
10.3.2	Xenon	281
10.4	Medical Carbonic Acid (Carbon Dioxide)	281
10.5	Medical Air	282
	<i>References</i>	282
11	Logistics of Industrial Gas Supply	283
11.1	Introduction	283
11.2	Storage and Transport of Compressed Gases	284
11.2.1	Fundamentals	284
11.2.2	Kinds of Transport and Storage for Compressed Gases	285
11.2.3	Efficiency of Compressed Air Gas Transport	286
11.3	Storage and Transport of Liquefied Compressed Gases	286
11.3.1	Fundamentals	286
11.3.2	Forms of Transport and Storage of Liquefied Gases	287
11.3.3	Efficiency of the Transport of Liquefied Gases	288
11.4	Special Forms of Supply	289
	<i>References</i>	289
	Subject Index	291

List of Contributors

Dr. Heinz Bauer

Linde AG
Geschäftsbereich Linde Engineering
LE-GD
Dr.-Carl-von-Linde-Strasse 6–14
82049 Pullach
Germany
Sections 7.1–7.6

Dr. Michael Berger

Linde AG
Geschäftsbereich Linde Gas
Carl-von-Linde-Strasse 25
85716 Unterschleißheim
Germany
*Sections 2.5, 3.6, 4.3, 5.4, 6.3,
7.7, 8.5*

Dr. Matthias Duisberg

Umicore AG & Co. KG
Bereich HC
Postfach 1351
63403 Hanau
Germany
Section 5.4.1.3

Dr. Heinz-Wolfgang Häring

Lommelstrasse 6
81479 München
Germany
Chapter 1

Dr. Harald Klein

Linde AG
Geschäftsbereich Linde Engineering
LE-HDV
Dr.-Carl-von-Linde-Strasse 6–14
82049 Pullach
Germany
Section 5.2

Dr. Matthias Meilinger

Linde AG
Geschäftsbereich Linde Engineering
LE-EC
Dr.-Carl-von-Linde-Strasse 6–14
82049 Pullach
Germany
*Sections 2.1, 2.3, 2.4, 3.1, 3.2, 3.5,
5.3, 6.1*

Johann Raab

Linde AG
Geschäftsbereich Linde Gas
LG-THA
Seitnerstrasse 70
82049 Pullach
Germany
Sections 8.1–8.4

Dr. Harald Ranke

Linde AG
Geschäftsbereich Linde Engineering
LE-HPP
Dr.-Carl-von-Linde-Strasse 6–14
82049 Pullach
Germany
Section 5.1

Jaco Reijkerk

Linde AG
Geschäftsbereich Linde Gas
Hydrogen Solutions
Seitnerstrasse 70
82049 Pullach
Germany
Section 5.4.1.2

Dr. Hans Schmidt

Linde AG
Geschäftsbereich Linde Engineering
LE-GDV
Dr.-Carl-von-Linde-Strasse 6–14
82049 Pullach
Germany
Sections 4.1, 4.2

Dr. Dirk Schwenk

Linde AG
Geschäftsbereich Linde Engineering
LE-LDV
Dr.-Carl-von-Linde-Strasse 6–14
82049 Pullach
Germany
Sections 2.2, 3.3–3.5

Dr. Hermann Stenger

Linde Gas
Therapeutics GmbH & Co. KG
Gas Solutions Hospital Care
Edisonstrasse 2
85716 Unterschleißheim
Germany
Chapter 10

Dieter Tillmann

Linde AG
Geschäftsbereich Linde Gas
LG-SEP
Seitnerstrasse 70
82049 Pullach
Germany
Sections 6.1, 6.2

Bernhard Valentin

Linde AG
Geschäftsbereich Linde Engineering
LE-BE
Dr.-Carl-von-Linde-Strasse 6–14
82049 Pullach
Germany
Chapter 11

Dr. Kurt Wilde

Sommerstrasse 1
82234 Weßling
Germany
*Sections 2.5, 3.6, 4.3, 5.4, 6.3, 7.7, 8.5,
Chapter 9*

Dr. Joachim Wolf

Linde AG
Geschäftsbereich Linde Gas
Hydrogen Solutions
Seitnerstrasse 70
82049 Pullach
Germany
Section 5.4.1.2

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).

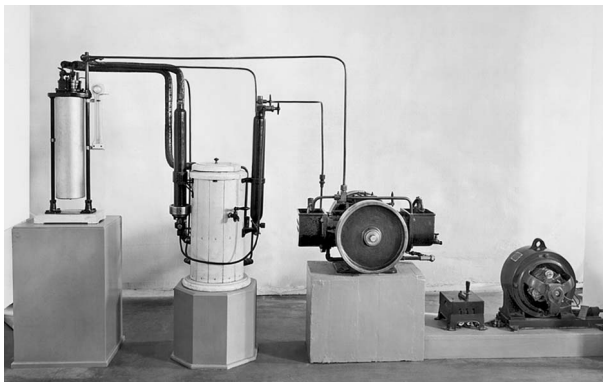


Fig. 1.1 Typical assembly of a Linde air liquefier (ca. 1899).

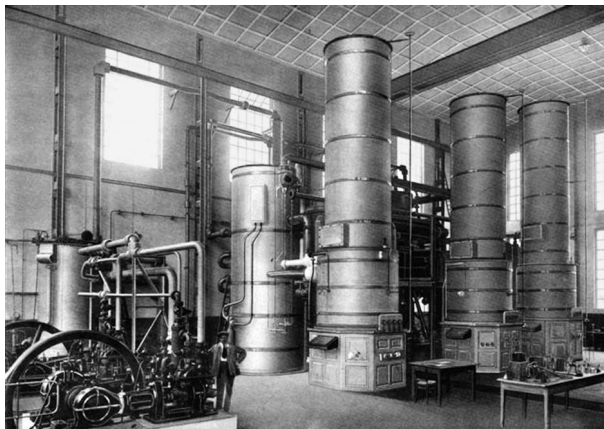


Fig. 1.2 Linde air separation unit for simultaneous production of $200 \text{ m}^3 \text{ h}^{-1}$ oxygen and $1,800 \text{ m}^3 \text{ h}^{-1}$ nitrogen (ca. 1919).

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 $3,500 \text{ td}^{-1}$, 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 $30,000 \text{ td}^{-1}$ 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 $40,000 \text{ td}^{-1}$ 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 <i>H. Cavendish</i>
1783	First flight of a hydrogen-filled balloon (<i>J. Charles</i>) using hydrogen generated from the reaction between iron and sulphuric acid
1853	<i>J. P. Joule</i> and <i>W. Thomson</i> 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 <i>Andrews</i>
1892	<i>H. Moissan</i> and <i>Th. L. Wilson</i> discover a method for generating calcium carbide in an electric furnace, enabling industrial production of acetylene in 1895
1895	<i>C. v. Linde</i> builds the first technical apparatus for the liquefaction of air
1898	Liquefaction of hydrogen by <i>J. Dewar</i>
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	<i>C. v. Linde</i> employs a rectification process for technical production of liquid oxygen
1902	<i>G. Claude</i> invents the piston expansion machine for air liquefaction
1908	Liquefaction of helium by <i>H. Kamerlingh-Onnes</i>

1910	<i>C. v. Linde</i> invents the double-column rectifier for simultaneous production of oxygen and nitrogen
1913	Technical ammonia synthesis from nitrogen and hydrogen by <i>F. Haber</i> and <i>C. Bosch</i> (BASF)
1917	First extraction of helium from natural gas in Hamilton, Canada
1922	Technical methanol synthesis from synthesis gas by <i>G. Patart</i> (BASF)
1925	Development of Fischer–Tropsch synthesis, i.e. catalytic synthesis of hydrocarbons using synthesis gas (mixture of hydrogen and carbon monoxide) by <i>F. Fischer</i> and <i>H. Tropsch</i> . 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

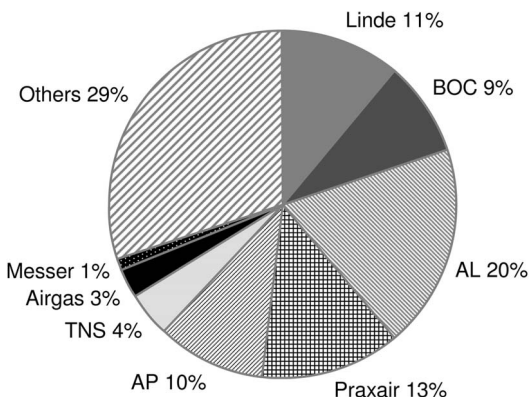


Fig. 1.4 Global market shares of industrial gas companies, 2005.

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).

References

- [1.1] C. Linde: *Aus meinem Leben und von meiner Arbeit* (1916), reprint Oldenbourg Verlag, Munich, 1979, p. 87.
- [1.2] W. Foerg: *The History of Air Separation*, MUST '96, Munich Meeting on Air Separation Technology, 1996, pp. 1–12.
- [1.3] E. Almqvist: *History of Industrial Gases*, Kluwer Academic/Plenum Publishers, New York, 2003.

- [1.4] Winnacker-Küchler, *Chemische Technologie*, Vol. 3: *Anorganische Technologie*, 4th edition, Carl Hanser Verlag, 1983, pp. 566–650.
- [1.5] W. Linde et al.: *The Invisible Industries/The Story of the Industrial Gas Industry*, International Oxygen Manufacturers Association (IOMA), Cleveland, OH 1997.
- [1.6] *Römpp*, 10th edition, Thieme Verlag, Stuttgart, 1997, p. 1915.
- [1.7] Spiritus Consulting Ltd.: *Annual Report 2005*, Cornwall, UK, 2006, www.spiritusgroup.com.
- [1.8] Datamonitor: *Global Industrial Gases Research Report*, 2005.
- [1.9] E. Gobina: *C-237 – The World Industrial Gas Business*, Business Communications Co., Inc., Norwalk, CT, Oct. 2003.
- [1.10] CryoGas Staff Report: *A Look at the Various Industrial Gas Associations*, Jan. 2003, pp. 28–35.
- [1.11] Compressed Gas Association (CGA): www.cganet.com.
- [1.12] European Industrial Gases Association (EIGA): www.eiga.org.
- [1.13] Industriegaseverband e.V. (IGV): www.industriegaseverband.de.

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 m² 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. N₂ 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 N₂ 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, N₂ is less soluble in water than O₂.

The inversion temperature of N₂ is 850 K. Inversion temperature is the temperature below which a gas cools down by adiabatic expansion (Joule-Thomson-Effect). Therefore, N₂ can be liquefied from room temperature by means of counter-cooling of previously expanded cold gas, in contrast to H₂ and 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. NH₃) to +5 (e.g. HNO₃). In the N₂-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 N₂ with other substances, e.g. through electric discharge or high temperature. Even at 3000 °C, there is no noticeable dissociation into the atoms ($K = c^2(\text{N}) / c(\text{N}_2) \approx 10^{-6}$). 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, N₂ 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-NH₂), amides (R-C(=O)-NH₂), nitriles (R-C≡N), oximes (R₂C=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 N₂-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.

- Cailletet 9, 141
 - calibration gas mixtures 261
 - fittings and pipes 272
 - production 264
 - production, dynamic-volumetric method 264
 - production, gravimetric method 265
 - production, manometric-static method 264
 - supply systems 273
 - can-type reformers 146
 - carbon dioxide
 - as greenhouse gas 186
 - high purity 195
 - liquefaction 193
 - liquid, properties 187
 - occurrence 185
 - pre-purification 191
 - properties 186
 - recovery 189
 - recovery from flue gas 198
 - sources 190
 - carbonic acid 185, 188
 - medical 281
 - carbonic acid anhydride 185
 - carbon molecular sieves, O₂ production 18
 - carbon monoxide
 - applications 182
 - occurrence 141
 - properties 141
 - carbonyl complexes 141
 - Caro 9
 - Cavendish 3, 9, 12, 136
 - CGA 6
 - Charles, C. 136
 - Charles, J. 3
 - chemical scrubbing 150
 - China Industrial Gases Industry Association (CIGIA) 7
 - CIGIA 7
 - Claude, G. 2, 3
 - Clement 141
 - CMS 18, *see also* carbon molecular sieves
 - CO 141
 - CO₂ 185
 - CO₂ reforming, synthesis gas production 144
 - CO₂ scrubbing 191, 192
 - CO₂ source 189
 - cold box 21, 23
 - columns, air separation 54
 - Commission Permanente Internationale (CPI) 6
 - compressed air for breathing apparatuses 282
 - compressed gas 287
 - liquefied, storage 286
 - liquefied, storage in cryogenic jugs 287
 - liquefied, storage in vertical tanks 287
 - pipeline 286
 - pipeline systems 286
 - Compressed Gas Association 6
 - compressed gas cans 285
 - compressed gas cylinder 283, 284
 - colour labelling 284
 - compressed gas cylinder bundles 285
 - compressed gas trailers 286
 - compressor, air separation 45
 - concentration units 262
 - convective reformer 149
 - crude argon column
 - air separation 26
 - McCabe–Thiele diagram 29
- d**
- D 137
 - Davy, E. 1, 240
 - Desormes 141
 - deuterium 137
 - Dewar 3, 136
 - Dirty Shift 150
 - dot notation, pure gases 256
 - dry ice 187
 - production 200
 - DVS 241
- e**
- EIGA 6
 - electronic gases 269
 - ethane, recovery from natural gas 229
 - ethene 249, *see also* ethylene
 - application in autogeneous engineering 249
 - recovery 249
 - ethylene, properties 249
 - ethyne 243, *see also* acetylene
 - European Dry Ice Association (EDIA) 6
 - European Industrial Gases Association 6
 - exergy
 - definition 35
 - loss 35
 - expansion turbines, air separation 48
 - external compression, oxygen recovery 33
 - Eyde 9

f

Fenske, formula by 30
 Fick's Law 16
 Fischer 4, 136
 Fischer-Tropsch synthesis 4, 136
 flooding in the downcomer 57
 Fontana, Felice 136
 Frank 9
 FT-synthesis 136
 fuel gases 239

g

GAN 2
 gas-to-liquid 238
 gas companies, shares in the world market 5
 Gases and Welding Distributors Association (GAWDA) 7
 gases in medicine 277
 gasification reactor 147
 gas mixtures 261
 – production 263
 Gas Subcooled Process 227
 GAWDA 7
 generator gas 135
 glycol scrubbing, natural gas 225
 GOX 2
 GOX med 278
 GSP 226, 227
 GTL 2, 238

h

Haber 4, 9
 heat exchanger
 – air separation 49
 – coil-wound 234, 235
 He I 127
 He II 127
 helium
 – high purity, recovery 128
 – liquefaction 130
 – occurrence 125
 – properties 127
 – recovery 127
 helium-method, age determination of minerals 125
 helium content, ambient air 125
 Henry's Law 16
 high-temperature shift 150
 Hoppe 112
 HTS 150
 HyCO-unit 158
 hydrogen
 – applications 164

– bridge bonds 140
 – frequency 137
 – heavy 137
 – normal 138
 – occurrence 136
 – ortho 137
 – para 137
 – production by electrolysis of water 143
 – properties 137

i

industrial gas companies 5
 industrial gases, supply, logistics 283
 Industriegasverband e.V. (IGV) 7
 instrumentation gases for analytical measuring methods 258
 internal compression, oxygen recovery 33
 International Oxygen Manufacturers Association (IOMA) 7

j

Japanese Industrial Gas Association (JIGA) 7
 jet flooding 57
 Joule, J. P. 3
 Joule-Thomson effect 1, 3

k

Kamerlingh-Onnes, H. 3, 125
 Kr/Xe
 – fine purification 115
 – fine purification, combustion of hydrocarbons at the catalyst 115
 – fine scrubbing 117
 – pre-enrichment in the air separator 113
 krypton 111
 – occurrence 111
 – recovery 112

l

Lasonne 141
 laughing gas, *see* nitrous oxide
 laughing gas for anaesthesia 280
 Lavoisier 11, 185
 Linde, C. v. 1, 3, 9
 Linde air liquefier 1
 Linde air separation 2
 Linz-Donawitz (LD) process 4
 liquefied natural gas 220
 liquefied petroleum gas 225
 – recovery from natural gas 225
 liquefiers 37
 liquid turbines, air separation 48
 LNG 220

- applications 238
 - low-pressure column, air separation 28
 - low-temperature shift 150
 - LOX 59
 - LOX med 278
 - LPG 225
 - LTS 150
- m**
- MAG 4
 - McCabe–Thiele diagram
 - binary O₂/Ar-mixture 29
 - crude argon column 29
 - MDEA 192
 - MEA 150, 191
 - Medical Device Directive, medical gases 278
 - medical gases 277
 - medium-temperature shift 150
 - membrane, nitrogen recovery 16
 - membrane module, parameters 17
 - metal hydrides 140
 - methanation 151
 - methane hydrate 218
 - methane scrubbing, cryogenic 155
 - methyldiethanolamine 192
 - as chemical solvent for synthesis gas 150
 - MFC process 234
 - Mikropor A 246
 - Mixed Fluid Cascade process 234
 - Moissan, H. 1, 3, 240
 - molecular sieves
 - for pressure swing adsorption 18
 - zeolitic, O₂ recovery 18, 20
 - mole fraction 262
 - monoethanolamine 191
 - as chemical solvent for synthesis gas 150
 - mtpa 231
 - MTS 150
- n**
- N₂ 10
 - nasal cannula 279
 - natural gas 217
 - basic feed for synthesis gas 136
 - calorific value 220
 - composition 223
 - dew-point adjustment 224
 - dry 220
 - ethane separation 229
 - glycol scrubbing 224
 - liquefaction 231
 - nitrogen separation 236
 - occurrence 218
 - occurrence, detected 218
 - separation from liquefied petroleum gas 225
 - treatment 224
 - wet 220
 - natural gas bubble 218
 - natural gas deposits 219
 - natural gas development 217
 - natural gas reserves 219
 - neon 111
 - occurrence 111
 - properties 112
 - recovery 118
 - recovery, fine purification 119
 - recovery, pre-enrichment 118
 - nitrogen
 - applications 67
 - chemical properties 10
 - fixation 10
 - history 9
 - inversion temperature 10
 - occurrence 9
 - properties 10
 - nitrogenase 10
 - nitrogen generators 36
 - nitrogen recovery
 - by means of PSA 19
 - membranes 16
 - nitrogen scrubbing 156
 - nitrous oxide, medical, processing 280
 - noble gas hydrates 112
 - normal-hydrogen 138
- o**
- OHR 228
 - OHR-process 228
 - OMA 7
 - ortho-hydrogen 137
 - oxygen
 - applications 83
 - concentrators 279
 - for medical application 278
 - history 11
 - inversion temperature 11
 - occurrence 11
 - properties 11
 - refining 12
- p**
- para-hydrogen 137
 - partial oxidation, production of synthesis gas 144, 146

Patart 4, 136
 peak-shaving plants, natural gas 231
 permeabilities of membranes 16
 photosynthesis 186
 PO 146
 PO-plant 160
 – gasification of heavy oil 159
 PO-reactor 147
 – Texaco 148
 polymeric membranes, gas separation 16
 potash as a chemical solvent for synthesis
 gas 150
 pre-reformer 158
 pressure column, air separation 25
 Pressure Swing Adsorber Unit
 – helium recovery 128
 pressure swing adsorption 18
 – nitrogen recovery 18
 – oxygen recovery 18
 – production of high-purity hydrogen
 from synthesis gas 151
 Priestley 9, 11, 141
 primary reformer 148
 process analytics, synthesis gas plants 161
 production of hydrogen, reformer plant
 157
 production of pure argon 29
 promoted combustion-test 61
 PSA 18, 151
 Puls Discharge Detector 120
 pure argon column, air separation 26
 pure gases 256
 – dot notation 256
 – fittings and pipes 272
 – supply systems 273

q

Q-T-Diagram 33
 quantum fluid 127
 quantum solid 127

r

radon, occurrence 111
 Ramsay 111
 Rayleigh, J. W. 12
 rectisol process 151
 rectisol scrubbing 151
 Recycle Split Vapor 229
 RSV 229, 230

s

Scheele 9
 secondary reformer 148
 separation factor 40, 114

SFR 227
 Shell-method, partial oxidation 147
 sieve tray columns, air separation 55
 Sirius-Linde, development system for
 acetylene 246
 specialty gases, disposal 271
 Split Flow Reflux 227
 steam reformer 145, 157, 159
 steam reforming, *see* steam reformer
 superfluid 127
 synthesis gas
 – applications 182
 – definition 135
 – generation by autothermal reforming
 148
 – generation by partial oxidation 146
 – generation by steam reforming 145
 – processing 150
 – processing, condensation process 154
 – processing, cryogenic processes 153
 – processing, membrane process 152
 – processing, methanation 151
 – processing, methane scrubbing 154
 – processing, removal of carbon dioxide
 150
 – production 143
 – production from hydrocarbons 144
 – removal of acid gases 150
 synthol-process 136

t

T 137
 tandem reformer 149
 Technical Rules for Compressed Gases 285
 Texaco-method, partial oxidation 147
 Texaco-process, partial oxidation 159
 thermosiphon and downflow evaporator 53
 Thilorier 185
 Thomson, W. 3
 TIG 4
 TRG 285
 tritium 137
 Tropsch 4, 136
 turbines, air separation 47
 turbo compressor, radial, air separation 45
 two-column nitrogen generator 36

v

vacuum pressure swing adsorption 20
 Verband der Chemischen Industrie e.V.
 (VCI) 7
 VPSA 20