

the ortho to the para form to prevent subsequent exothermic conversion and evaporation of the product in storage. The heat of conversion (703 J) is great enough, compared with the heat of vaporization (444 J), to cause considerable loss.

An interesting development is the use of semipermeable membranes either to produce pure hydrogen or to adjust the gas stream composition. Hollow fibers of polysulfone covered with a proprietary coating (Monsanto's Prism system) are used for the membranes. The separator consists of a bundle of fibers (10,000 to 100,000) oriented vertically that is capped at one end and placed on an open epoxy tube sheet on the other. The fibers are 800  $\mu\text{m}$  in diameter or less and the whole vessel is 10 or 20 cm in diameter by 3 m long. The separation of the components of the entering gas is determined by the rates at which the substances permeate the membrane. The modules can be run in series or parallel to attain high purities or to vary the composition of synthesis gas. One application is the production of 1.3/1  $\text{H}_2/\text{CO}$  gas for oxo alcohol manufacture from 3.1/1  $\text{H}_2/\text{CO}$  gas.<sup>22</sup>

## OXYGEN AND NITROGEN

**USES AND ECONOMICS.** In 1981 the production of oxygen in the United States was  $11.75 \times 10^9 \text{ m}^3$ . This represented a drop from 1979 and 1980, and for the second year in a row nitrogen production exceeded that of oxygen.<sup>23</sup>

Oxygen is produced by the liquefaction and rectification of air in highly efficient, well-insulated, compact plants or by the pressure-swing adsorption system. Supply of raw material is not a problem and, because transportation of the product adds considerably to the cost, plants are usually located close to the point of consumption.<sup>24</sup> An air separation plant may be located on the customer's property and, as such, is known as an on-site plant. It may be owned and operated off site by the designer and builder of the plant and the product delivered by a short pipeline. At some air separation complexes, several customers are serviced by a single pipeline many kilometers in length. In such cases, oxygen assumes many of the characteristics of a utility.

Air separation plants vary in size from small cryogenic units producing less than 1 t/day to giant plants producing more than 1800 t/day (Fig. 4.4). PSA plants operate in the size range of 13 kg to 27 t/day. The bulk of the oxygen is produced at high purity (99.5%). Low purity usually refers to the 95 to 99% purity range. For high-purity oxygen, the impurities are argon and traces of rare gases, hydrocarbons, and carbon dioxide.

A major use of oxygen is<sup>25</sup> the production of steel in open-hearth or basic oxygen furnaces. The steel industry also uses oxygen for removal of scale from billets by an oxyacetylene flame and in oxygen lances for cutting out imperfections. The chemical industry<sup>26</sup> is a large con-

<sup>22</sup>MacLean and Graham, Hollow Fibers Recover Hydrogen, *Chem. Eng.* 87 (4) 54 (1980) Unique Membrane System Spurs Gas Separation, *Chem. Eng.* 88 (24) 62 (1981).

<sup>23</sup>Key Chemicals, Oxygen, *Chem. Eng. News* 60 (29) 21 (1982).

<sup>24</sup>ECT, 3d ed., vol. 16, 1981, p. 653; vol. 15, 1981, p. 932.

<sup>25</sup>Wolff, Eyre, and Grenier, Oxygen Plants: 10 Years of Development and Operation, *Chem. Eng. Prog.* 75 (7) 83 (1979).

<sup>26</sup>Gans, Choosing Between Air and Oxygen for Chemical Processes, *Chem. Eng. Prog.* 75 (1) 67 (1979).

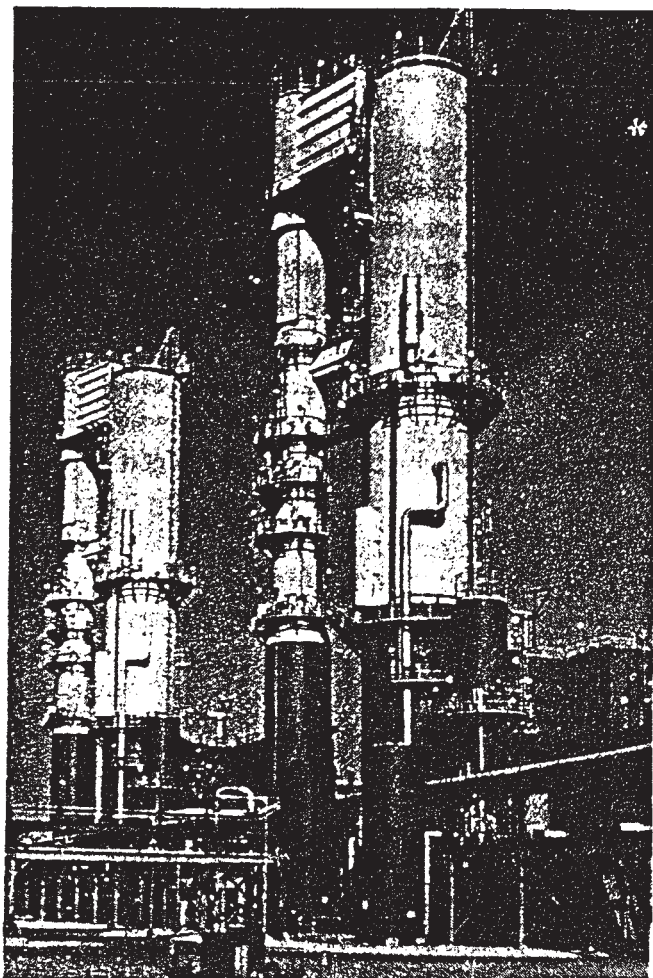


Fig. 4.4. Cryogenic oxygen plant producing 1800 t/day at Burns Harbor, Ind. (Union Carbide Corp., Linde Div.)

sumer of oxygen, using it in such applications as acetylene and ethylene oxide production and in ammonia and methanol production via partial oxidation of hydrocarbons.

Other uses include metalworking applications, underground gasification and fireflooding, enhancement of combustion processes in nonferrous metallurgical processes, medical purposes in hospitals, and aviators' breathing oxygen. In an aerospace application, the first stage of the Saturn V rocket required  $1.5 \times 10^6$  kg of liquid oxygen for fuel oxidation. Consumption for this purpose by NASA peaked in the mid-1960s at about  $280 \times 10^6$  m<sup>3</sup>/year and has since declined with the completion of the Apollo program. The greatest new potential use for oxygen is in synthetic fuels production: coal gasification and coal liquefaction. It is predicted that by 1990 the amount used for this could surpass that used for steel.

Environmental and energy problems are producing new applications for oxygen. Municipalities as well as industry are now aerating wastewater streams with oxygen instead of air in the activated sludge process for secondary treatment.<sup>27</sup> Oxygen is also used for the disposal and conversion of refuse to usable by-products.

Nitrogen became the largest-volume industrial gas in 1981 with the production of  $13.6 \times 10^9$  m<sup>3</sup>.<sup>28</sup> The major use of nitrogen is as a gaseous blanket that excludes oxygen and moisture.

<sup>27</sup>Direct Oxygenation of Wastewater, *Chem. Eng.* 78 (27) 66 (1971); see Chap. 3.

<sup>28</sup>Key Chemicals, Nitrogen, *Chem. Eng. News* 60 (29) 22 (1982); Schell, A Buoyant Industrial Gas Industry Faces the Future, *Chem. Business* May 4, p. 18, 1981. The Air-Gas Merchant Market Heats Up, *Chem. Week* 132 (5) 49 (1983).

**Table 4.5** Properties of Air and Constant Constituents

Gas	Volume %	Triple Point, K	Boiling Point, K	Critical Temp., K	Critical Pressure, MPa
Nitrogen	78.084	63.156	77.35	128.2	3.39
Oxygen	20.946	54.363	90.19	154.58	5.04
Argon	0.934	83.78	87.27	150.8	4.81
Hydrogen	0.00005	13.96	20.27	33.19	1.29
Neon	0.001921	24.55	27.09	33.19	2.68
Helium	0.0005239	*	4.215	5.20	0.22
Krypton	0.0001139	115.95	119.81	209.4	5.40
Xenon	0.0000087	161.3	165.04	289.8	5.74
Carbon dioxide	0.02-0.04	216.6	194.68†	304.2	7.25

\*Has no triple point.

†Sublimation temperature.

SOURCE: Scott, *Cryogenic Engineering*, Van Nostrand, New York, 1962, pp. 268-321; Mirtov, *Gaseous Composition of the Atmosphere and Its Analyses*, transl. NASA TTF-145, OTS 64-11023, U.S. Dept. Commerce, 1964.

For this, it must be dry and have an extremely low oxygen content (less than 10 ppm). The other use is for obtaining extremely low temperatures, down to  $-210^{\circ}\text{C}$ . The largest consumption of nitrogen is in the manufacture of ammonia. Production statistics usually do not include this usage because the nitrogen usually originates from feedstock and air rather than from merchant nitrogen. Other uses by the chemical industry are in applications to exclude oxygen or moisture, such as blanketing of polymerization processes, or for applications as a diluent, for example, in the control of reaction rates. It is replacing traditional blanketing agents, such as natural gas, in the manufacture of electronic products.

It is extensively used by the steel industry for blanketing and bright-annealing. The food processing industry uses nitrogen for food freezing and as a refrigerant in the processing and refrigerated transport of frozen foods. Other uses for liquid nitrogen include low-temperature metal treatment, shrink-fitting of parts, deflashing of molded plastic and rubber parts, and in cryobiology for storage of biological materials such as whole blood and bull semen, and as a refrigerant in cryosurgical procedures.

A new, rapidly growing use of nitrogen is for tertiary oil recovery in old oil fields. The gas is used to maintain pressure in the wells. This was formerly done with natural gas. It is usual to use merchant nitrogen for this purpose until it proves to be satisfactory. When it is, an on-site producing plant is constructed.

**MANUFACTURE.** Oxygen and nitrogen are produced principally by the liquefaction and rectification of air.<sup>29</sup> Production by the electrolytic dissociation of water is of little significance. Air is a mixture of many substances, of which eight are found in unvarying concentration; seven of these are of commercial importance. Table 4.5 lists the major constituents of air and their properties.

The production of high-purity gaseous oxygen from air via the cryogenic process is illustrated by the flowsheet in Fig. 4.5. Filtered air is compressed to approximately 520 kPa in a centrifugal compressor and aftercooled. After separating out any liquid water, the air enters the reversing heat exchanger and is cooled to near its dew point in countercurrent heat

<sup>29</sup>Latimer, Distillation of Air, *Chem. Eng. Prog.* 63 (2) 35 (1967) (extensive treatment of air separation technology); Advances in Large Scale Oxygen Production, *Adv. Pet. Chem. Refin.*, vol. 9, chap. 1, Interscience, New York, 1964.

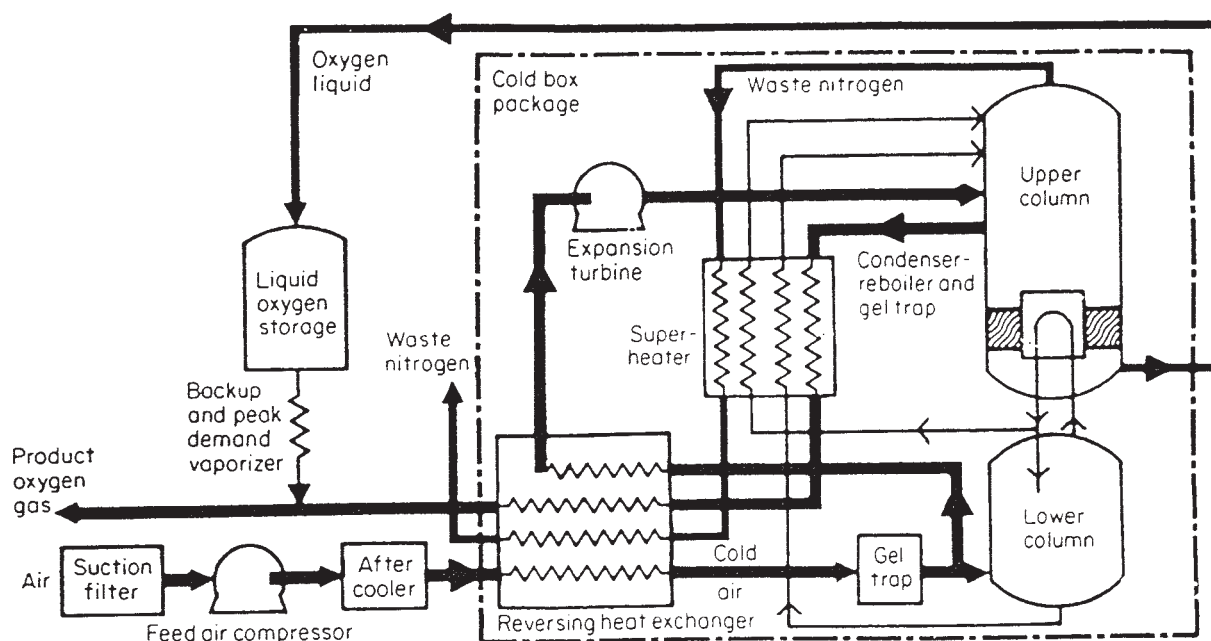


Fig. 4.5. Flowchart for on-site air separation unit. (Union Carbide Corp., Linde Div.)

exchange with the outgoing gaseous products. As the air cools, moisture is first condensed and frozen on the walls of the heat exchanger passage. At lower temperatures carbon dioxide freezes and is also deposited on the heat exchanger passage walls. The air emerging from the reversing heat exchanger is completely dry and has had over 99% of the carbon dioxide removed. Gas-phase, fixed-bed adsorption is used to remove the remaining carbon dioxide and, more importantly, any hydrocarbons entering with the air which would be hazardous in the presence of liquid oxygen. The cleaned air is then fed to the bottom tray of the lower column of the double-column rectifier. This is shown in more detail in Fig. 4.6.

The double-column rectifier consists of two tray-type distillation columns which are thermally connected at the center through a heat exchanger, which serves as a condenser for the lower column and a reboiler for the upper. Because nitrogen is more volatile than oxygen, it will ascend each column and oxygen will descend. Thus, on the reboiler side of the upper column, there is a pool of high-purity, boiling, liquid oxygen, while on the condenser side of the lower column, nearly pure nitrogen is being condensed. Because the normal boiling point of oxygen is  $12.8^{\circ}\text{C}$  higher than that of nitrogen, the pressure in the lower column must be high enough to raise the condensing temperature of nitrogen sufficiently to provide a positive temperature-driving force in the main condenser. The condensed nitrogen is split as it leaves the main condenser; one portion returns to the lower column as reflux, and the other is diverted to the upper column, through the nitrogen superheater, also for use as reflux. An oxygen-rich (35%) liquid stream leaves the bottom of the lower column and, after being subcooled in the nitrogen superheater, serves as the main feed stream for the upper column. The two liquid streams entering the upper column are first subcooled to reduce flashing when throttled to the lower pressure of the upper column. The oxygen product is removed as saturated vapor from the main condenser, and a high-purity nitrogen product is removed as saturated vapor from the top of the upper column. The remaining gas is removed as a low-purity waste nitrogen stream several trays from the top of the upper column.

Carbon dioxide and light hydrocarbons tend to accumulate in the liquid oxygen in the main condenser. These constituents are removed by recirculating the main condenser liquid through a silica gel adsorption trap to prevent the buildup of carbon dioxide and hazardous hydrocarbons.



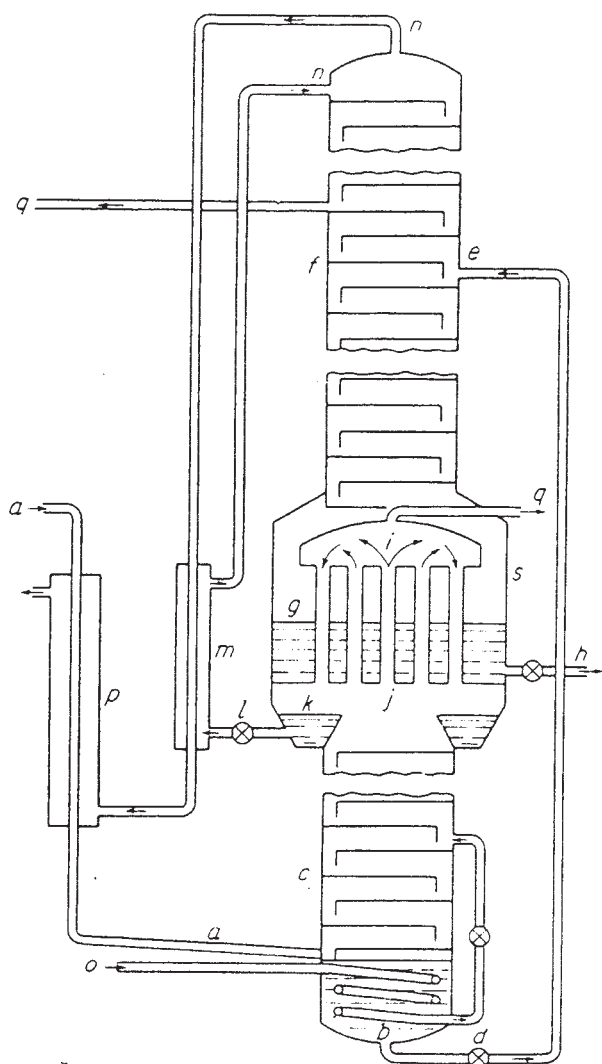


Fig. 4.6. Diagram of Linde double column and main condenser. The rectifier separates liquid air into the more volatile nitrogen (bp 77.4 K) and the less volatile oxygen (bp 90.2 K). (a) cold-air feed at 582 to 651 kPa; (b) kettle liquid rich in oxygen (about 35% O<sub>2</sub>); (c) lower or high-pressure column (582 to 651 kPa); (d) throttling valve for kettle liquid; (e) liquid feed to upper column; (f) upper or low-pressure column (122 to 183 kPa); (g) accumulated oxygen liquid; (h) exit for product oxygen, 99.5% pure; (i) plate-and-fin main condenser-reboiler; (j) liquid nitrogen reflux to lower column; (k) liquid nitrogen reflux to upper column; (l) throttling valve for nitrogen reflux; (m) plate-and-fin heat exchanger, liquid-nitrogen reflux and kettle liquid to product nitrogen and waste nitrogen; (n) cold nitrogen vapor to main condenser. (o) cold exhaust air from expansion turbine; (p) cold product nitrogen gas; (q) cold waste nitrogen. (Union Carbide Corp., Linde Div.)

The two nitrogen and the oxygen streams are superheated to approximately 100 K in their respective superheaters and are delivered to the reversing heat exchangers for warm-up to the ambient temperature in heat exchange with the incoming air. The high-purity nitrogen and high-purity oxygen are warmed in separate nonreversing passages, while the waste nitrogen flows through passages which periodically reverse with the air passages. The waste nitrogen thus flows past the solid carbon dioxide and frozen moisture previously deposited from the air and causes the deposits to sublime into the waste nitrogen and to be carried out of the heat exchanger. Periodic reversal of the air and waste nitrogen passages ensures that the heat exchanger is maintained in a clean, operable condition.

Refrigeration to overcome heat influx to the process is provided by expanding a portion of the air stream through a centrifugal expansion turbine. Ideally, this is an isentropic process which reduces the enthalpy of the air being expanded and rejects the energy from the process via the turbine shaft. Usable work can be recovered by coupling an electric generator, for example, to the turbine shaft. Clean, cold air for the turbine is withdrawn downstream of the absorber and reheated in a separate passage of the reversing heat exchanger to the proper temperature for introduction to the turbine. The reheating also serves to control the temperature pattern to help maintain clean operation of the reversing heat exchanger. Air exhausting from the turbine is fed to the proper tray of the upper column.

Heat exchangers are usually of the very compact brazed aluminum plate-and-fin construction. Distillation trays may be either perforated or bubble cap. Materials of construction are

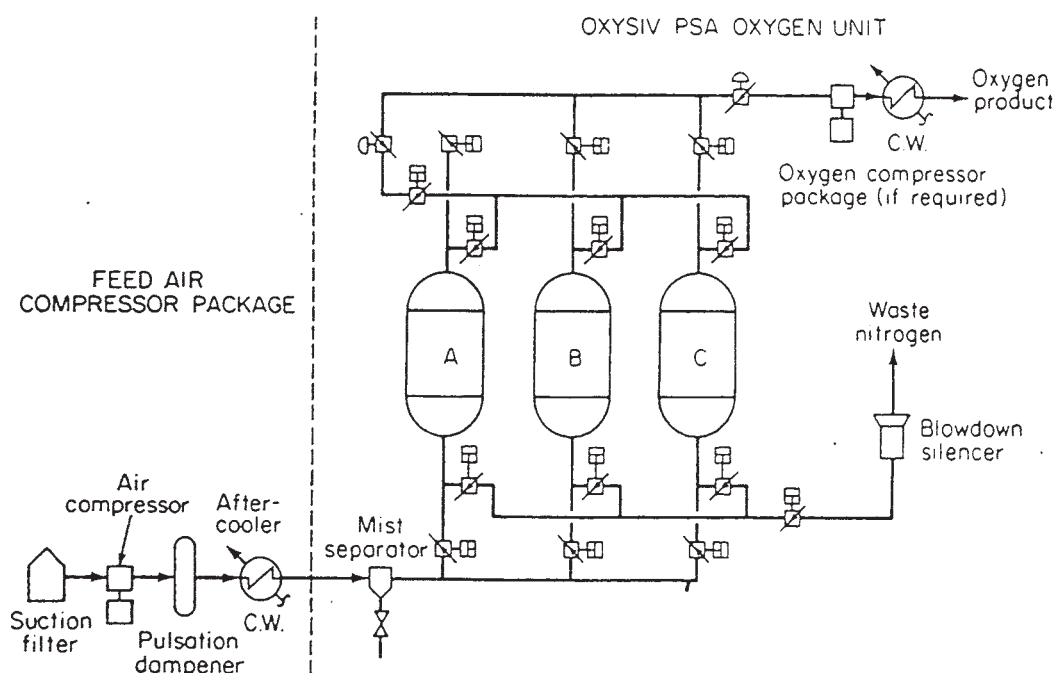


Fig. 4.7. Pressure-swing generation system, Union Carbide's "Oxysiv" PSA oxygen generation system.

aluminum, stainless steel, copper, and copper alloys. All low-temperature equipment is assembled, with piping, in one or more cold boxes heavily insulated with nonflammable materials.

Some oxygen is produced by a noncryogenic, pressure-swing adsorption process<sup>30</sup> using a molecular sieve as the adsorbent to separate oxygen from ambient temperature compressed air. This process produces oxygen ranging in purity from 90 to 95% in the capacity range of 1 to 60 t/day. This simple process eliminates the need for cryogenic equipment, feed dryers, regeneration heaters, and attendant utility and maintenance costs.

Union Carbide's patented PSA process (U.S. Patent 3,738,087) uses three vessels. In operation, each vessel cycles between two stages—adsorption and regeneration. One vessel adsorbs while the others regenerate, as shown in Fig. 4.7. When the adsorbing vessel achieves its capacity for impurities, the compressed air feed is automatically switched to another vessel. The first vessel then begins its regeneration cycle, which is accomplished in three successive steps: depressurizing, purging with product oxygen, and partial repressurization, after which the vessel is again ready for the adsorption stage.

Impurities are rejected during the depressurization and purge steps and vented into the atmosphere. Regeneration is completed at atmospheric pressure. Adsorption and regeneration are automatic and rely only upon pressure swings for operation. There is no need for costly heating or refrigeration. Automatic timers, pressure switches, and relays control cycling as well as product flow.

## RARE GASES OF THE ATMOSPHERE

Oxygen and nitrogen are the primary components of the atmosphere, but air also contains nearly 1% argon and lesser amounts of neon, krypton, and xenon (Table 4.5). Argon, neon,

<sup>30</sup>Davis, Oxygen Separated from Air Using Molecular Sieve, *Chem. Eng.* 79 (23) 88 (1972); Shaner, *Production of Industrial Gases from the Air*, Union Carbide Corp. publication L-10000.

krypton, and xenon are all produced commercially as by-products from large cryogenic air separation plants. The distillation of liquid air is normally performed in the double-column arrangement illustrated in Fig. 7.6. The rare gases are produced in side columns operated in conjunction with the standard double-column plant.

A combination of a double column and side rectification columns is used to produce argon. Since argon boils at a temperature just below oxygen, its concentration level builds up in the upper column at a point above the oxygen product level. The argon-rich vapor is withdrawn from the upper column at a point about one-third of the distance between the oxygen product and the nitrogen waste and is fed to a side argon column. The feed vapor is primarily an argon-oxygen mixture (with some nitrogen) and because of the close boiling points of the components, the argon column is operated at a relatively high reflux ratio. The liquid reflux from the argon column is returned to the upper column at the same point as the vapor withdrawal. The crude argon product is withdrawn from the top of the argon column. The side argon column is driven by expanded kettle liquid obtained from the bottom of the lower column. The vaporized kettle vapor is fed to the upper column at the same point as the low-pressure turbine air feed. The argon column condenser usually includes a small liquid drain to the upper column. The purpose of this liquid drain is to avoid hydrocarbon buildup in the argon condenser liquid reservoir, since this condenser is not protected by hydrocarbon adsorption traps, as is the case with the main plant condenser. All process streams handled by the argon column are returned to the main plant columns, with the exception of the crude argon product. The crude argon is further processed in a section of the plant usually referred to as the argon refinery. The crude argon product contains oxygen and nitrogen impurities. The oxygen impurity is removed by the addition of hydrogen and subsequent catalytic combustion and gas drying to recover the water. The nitrogen impurity is removed by another distillation step that produces the refined argon product at a purity of 99.999%.

The primary application of argon is in metallurgical processes. One major use is as a shielding gas (from oxygen) in the welding of metals such as aluminum and stainless steel and in the refining of exotic metals such as zirconium, titanium, and many alloys. Another significant use of argon is as a filler gas for incandescent light bulbs. The chief process for the production of stainless steel is the "argon-oxygen decarburizing" process, which requires large quantities of argon.

Since neon boils at a considerably lower temperature than nitrogen, it normally collects in the dome of the main condenser as a noncondensable gas. It can be recovered by the addition of a side column. Neon has well-known applications as a filler gas for display lights. Much larger quantities are used in high-energy research. It is also finding increasing uses in instrumentation and as a safe low-temperature cryogen for specialty applications. A new use is evolving in deep-sea diving, where mixtures of neon and helium have shown many advantages.

Since krypton and xenon have high boiling points relative to oxygen, they normally accumulate in the liquid oxygen sump of the upper column of the main plant. The primary application of krypton is as a light bulb filler gas. Its thermal properties are more favorable than those of argon and lead to more effective light bulbs. Additionally, both krypton and xenon are used in instrumentation and research applications.

The very rare gases, neon, krypton, and xenon, are normally marketed by the industry as "specialty gases." Other specialty gas products include gases of unusually high purity for research purposes, instrumentation calibration standards, and special mixes serving the need of a specific industry or laboratory. Specialty gas departments of the industrial gas companies have several unique capabilities. Creating gas mixtures tailored to user requirements for purity and for accuracy of mixture formulation is one such capability. Packaging gases in any desired quantity is another capability. Shipments can be made throughout the range from a

single gaseous liter packaged in a glass bulb to highway tube trailers transporting 2800 m<sup>3</sup> and up. Also available is specialized equipment including valves, pressure and flow gages, regulators, etc., capable of metering and measuring gases with exceptional accuracies with minimal loss and without contamination.

## HELIUM

The helium industry began with the discovery of helium at Dexter, Kan. about 1900, but it is now also available from certain fields located in Oklahoma and Texas. The first pilot plants were constructed to supply helium for the lighter-than-air airships of the Allies in World War I to replace highly flammable hydrogen. Helium has 92.5 percent of the lifting power of hydrogen. Another less widely known use has been in a mixture with oxygen to provide a synthetic atmosphere for deep-sea divers and tunnel workers. Substitution of helium for nitrogen prevents nitrogen narcosis, which occurs at water depths greater than 30 m.

In aerospace applications, helium is employed to purge and pressurize spacecraft. This was the largest market for helium in the mid-1960s.<sup>31</sup> Since then, there has been a rise in the relative importance of other markets, such as protective atmospheres in the fabrication of titanium, zirconium, and other metals, the growing of transistor crystals, and as a shielding gas for welding. Other uses include lead detection, cryogenic applications, and for generating ultra-low-temperature environments for superconducting devices. The annual consumption increased from  $7.8 \times 10^6$  m<sup>3</sup> in 1962 to  $26.9 \times 10^6$  m<sup>3</sup> in 1966 and then declined steadily to  $12.7 \times 10^6$  m<sup>3</sup> in 1971. Consumption in 1980 in the United States was estimated at  $18.2 \times 10^6$  m<sup>3</sup>. The United States supplies 80 percent of the world's consumption and exports account for about one-quarter of domestic production. The Interior Department, in a government conservation program, is storing crude helium in underground reservoirs and, by 1981,  $1.13 \times 10^9$  m<sup>3</sup> was stockpiled. This conservation effort is necessary because the helium is lost to the atmosphere when natural gas is consumed. Extraction of helium from the atmosphere would be extremely expensive. It is generally agreed that this valuable resource should be recovered and stored until the time that new energy technologies require vast amounts of helium. For various reasons, both governmental policy and economic, the Interior Department stopped purchasing helium from private producers in 1973. Since that time a lot of helium has been vented to the atmosphere. In an effort to stop this waste, a bill was introduced into Congress in 1980 to mandate that the Interior Department acquire helium for storage either by separating it from the government's Tip Top field or by purchasing it from private companies, or both. The bill set a storage goal of  $1.8 \times 10^9$  m<sup>3</sup> by the end of 1985 and  $2.4 \times 10^9$  m<sup>3</sup> by 1990.<sup>32</sup>

In 1981  $6 \times 10^6$  m<sup>3</sup> of helium was produced and distributed to support federal programs such as NASA's space shuttle launches, the Department of Defense's advanced weapons research, and the Department of Energy's next-generation energy-conversion research. Of the gas thus distributed  $2.8 \times 10^6$  m<sup>3</sup> was extracted from natural gas and  $3.2 \times 10^6$  m<sup>3</sup> was

<sup>31</sup>Chopey, What's Next For Helium? *Chem. Eng.* 81 (12) 40 (1974).

<sup>32</sup>Anderson, Congress Renews Helium Conservation Effort, *Chem. Eng. News*, 58 (23) 11 (1980); Helium Conservation Drains Federal Funds, *Chem. Eng. News*, 47 (51) 46 (1969); ECT, 3d ed., vol. 12, 1980, pp. 249-287.



withdrawn from the Cliffside Gas Field which supplies the government reservoirs. Mobil Oil completed two wells in 1979 and 1980 in the Tip Top field in Sublette, Wyo. These wells are not currently in production, but the reserves in this field are estimated at  $1.42 \times 10^9 \text{ m}^3$ . Almost all of the Tip Top field is on federal lands.

A typical plant removes the 2% helium from the natural gas in the pipeline that crosses the site, with an extraction efficiency of 92 to 95 percent. The pipeline gas enters at 3 to 4.5 MPa, is first scrubbed to take out water and condensable hydrocarbons, and is then passed through a gas cleaner, which removes pipeline dust. From the cleaner, the gas goes to absorption towers, where  $\text{CO}_2$  is removed by a solution of MEA and diethylene glycol, and finally passes through a bauxite dryer. For the crude-helium-separation step, the purified gas enters large boxlike units, 12 m high with a cross section of 3 by 3 m, that operate in parallel. After entering one of the units, the gas is first chilled to  $-156^\circ\text{C}$  by heat exchange with the exiting crude helium and depleted natural gas. The chilled stream is expanded into a separator-rectifier column, where, with the aid of a side stream of cold low-pressure nitrogen in a coil, the natural gas is liquefied and separated. The rectified, or crude-helium gas (75% helium, 25% nitrogen), passes through a heat exchanger counter to the incoming gas.

The depleted natural gas as a liquid passes from the bottom of the separator-rectifier through an expansion valve and also helps chill incoming feed gas, after which it leaves the unit, is compressed, and then returns to the gas pipeline. To provide cooling and to be usable in a cold side stream, high-pressure nitrogen is chilled by expansion and split into two parts. One of these is further cooled to about  $-179^\circ\text{C}$  by expansion through two centrifugal turbo expanders located outside the separation unit box, and this cold stream then further chills the unexpanded portion of the original nitrogen stream.

To purify the crude-helium gas, the trace of hydrogen is first removed in a reactor with a small amount of air, where it is oxidized to water over a platinum catalyst. The hydrogen-free gas is further purified utilizing a pressure-swing adsorption (PSA) process. The PSA unit removes essentially all contaminants to very low levels, usually less than 10 ppm. Neon, however, is not removed by the PSA process, but for most helium uses it is not considered a contaminant.

Plants<sup>33</sup> are in operation to supply liquid helium (bp  $-268.9^\circ\text{C}$  at 101 kPa compared with  $-252^\circ\text{C}$  for hydrogen). The first plant at Amarillo, Texas produced 100 L/h. The Linde Division of Union Carbide Corp. assembled its plant inside a Dewar (i.e., thermos bottle) type of vessel 6 m high and 2.7 m in diameter. The difficulty is that *compressed helium does not exert the Joule-Thomson cooling effect upon expansion until  $-267^\circ\text{C}$  is reached*. Helium gas is compressed to 1.9 MPa at  $27^\circ\text{C}$  where it enters the Dewar cold box. Here it is cooled to  $-187^\circ\text{C}$  in the first of three fin-type aluminum heat exchangers against recycle helium and cold ( $-193^\circ\text{C}$ ) gaseous and liquid nitrogen. Next trace impurities are removed in a gel trap, and the gas stream is further cooled to  $-248^\circ\text{C}$  in a heat exchanger against recycle helium. The effluent is split into two streams, so that the large stream can cool by expanding from 1.8 MPa to 27 kPa in an expander engine, thereby cooling itself to  $-260^\circ\text{C}$  and thus providing a heat-exchange medium for further chilling the smaller fraction. Finally, the combined stream is chilled to  $-267^\circ\text{C}$  by the recycle stream. Here the Joule-Thomson effect is positive and, by expanding from 1.8 MPa to 31 kPa, the helium cools itself in a separating vessel to liquefy about 15 percent of the helium at  $-268^\circ\text{C}$ . The helium gas is recycled.

<sup>33</sup>Chopey, Liquid-Helium Plant Tackles Gas That's Hardest of All to Liquefy, *Chem. Eng.* 69 (20) 76 (1962); Liquid Helium Plant, *Chem. Eng.* 70 (15) 86 (1963); Haul Helium Faster, *Chem. Week* 99 (8) 57 (1966).

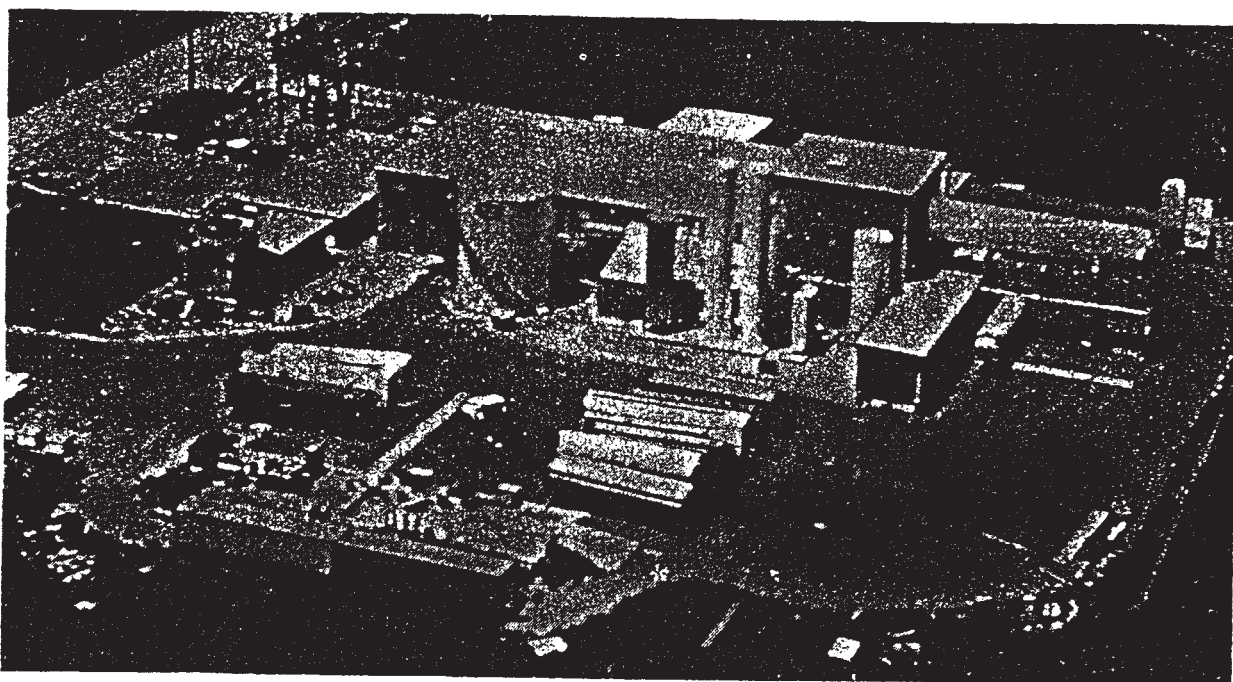


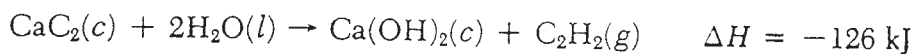
Fig. 4.8. Union Carbide's Linde helium production plant, Bushton, Kan.

The liquid-helium plant of the Kansas Refined Helium Co. at Otis, Kan. has an annual capacity of  $6.1 \times 10^6$  L of liquid helium. This plant supplies the Air Reduction Co. (Airco) with liquid helium for distribution nationally. Airco has 38,000-L trailer trucks as well as special cryogenic containers for delivering this helium. Linde Division of Union Carbide Corp. has a plant at Bushton, Kan. as shown in Fig. 4.8.

## ACETYLENE

**USES AND ECONOMICS.**<sup>34</sup> Acetylene is employed with oxygen to give a high welding temperature and in the manufacture of industrial chemicals such as vinyl chloride, acrylonitrile, polyvinylpyrrolidone, trichloroethylene, and acetic acid. Some of these compounds are also derived from other sources such as ethylene; only one chemical is made mostly from acetylene: chloroprene and its polymer neoprene. Studies of acetylene reactions at high pressures (the Reppe high-pressure technique) are very significant in that vinylation, ethynylation, and polymerization reactions have opened up a new field of chemistry by introducing many new compounds.

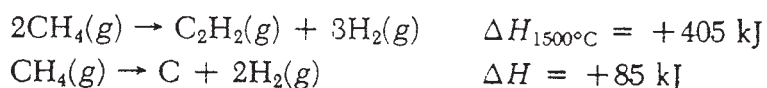
**MANUFACTURE.** Until recently all acetylene was made by the reaction of calcium carbide with water:



<sup>34</sup>Acetylene, *Chem. Eng. News* 40 (29) 54 (1963) (excellent use and production data); Miller, *Acetylene*, vol. 1, Academic, New York, 1965; Hardie, *Acetylene Manufacture Uses*, Oxford, New York, 1965; Sittig, *Acetylene Processes and Products*, Noyes, Park Ridge, N.J., 1968; Lorber et al., Acetylene Recovered from Ethylene Feedstock, *Chem. Eng.* 78 (15) 33 (1971); Baur, Acetylene from Crude Oil, *Chem. Eng.* 76 (3) 82 (1969) (process flowsheet); Acetylene from Coal Soon, *Chem. Eng.* 76 (6) 76 (1969).

There are two principal methods for generating acetylene from calcium carbide. The batch carbide-to-water, or wet, method takes place in a cylindrical water shell surmounted by a housing with hopper and feed facilities. The carbide is fed to the water at a measured rate until exhausted. The calcium hydroxide is discharged in the form of a lime slurry containing about 90% water. For large-scale industrial applications "dry generation," a continuous process featuring automatic feed, is popular. Here 1 kg of water is used per kilogram of carbide, and the heat of the reaction (6.2 MJ per cubic foot of acetylene) is largely dissipated by water vaporization, leaving the by-product lime in a dry, fairly easily handled state. Part of this can be recycled to the carbide furnaces. Continuous agitation is necessary to prevent overheating, since the temperature should be kept below 150°C and the pressure lower than 204 kPa.

The newest methods of manufacturing acetylene are through the *pyrolysis*, or *cracking*, of *natural gas* or liquid hydrocarbon feeds. The processes of most interest include partial oxidation, using oxygen, thermal cracking, and an electric arc to supply both the high temperature and the energy. An electric-arc procedure was used commercially at Huels, Germany. The free energy of acetylene decreases at higher temperatures. At 1600 K (1327°C) and higher, acetylene is more stable than other hydrocarbons<sup>35</sup> but decomposes into its elements. Hence conversion, or splitting, time must be incredibly short (milliseconds). The amount of energy needed is very large and in the region of the favorable free energy.



However, the decomposition of CH<sub>4</sub> into its elements starts at 850 K (578°C), hence competes with its degradation to acetylene. To lessen this degradation after raising the CH<sub>4</sub> (or other hydrocarbon) to a high temperature of about 1500°C for milliseconds, the reaction mass must be water-quenched almost instantaneously. Many flowcharts with technical data are depicted in ECT (loc. cit.) and also in the *1979 Gas Processing Handbook*.<sup>36</sup>

The partial combustion of natural gas is probably the method most used by experienced chemical manufacturers (Union Carbide, Tennessee Eastman, Monsanto, American Cyanamid, and Rohm & Haas). This is presented as a flowchart in Fig. 4.9 and embodies the chemical conversions just given. The process can be broken down into the following coordinated sequences:

Oxygen (90 to 98%) and natural gas are preheated separately to about 650°C, using fuel gas.

The two hot gases are conducted to and mixed in a burner or converter in a molar ratio of 0.60:100 for oxygen-methane.

The furnace or burner for this partial combustion consists of three parts: a mixing chamber, a flame or chemical-conversion zone, followed by a quench chamber with quench oil or water sprays. The chemical conversion is an almost instantaneous partial (two-thirds) combustion of the methane.

<sup>35</sup>ECT, 3d ed. vol. 1, 1978, pp. 211-243 (tables and other thermodynamic and technical data); Leroux and Mathieu, Kinetics of the Pyrolysis of Methane to Acetylene, *Chem. Eng. Prog.* **57** (11) 54 (1961); Acetylene Flame Technology, *Chem. Eng. Prog.* **61** (8) 49-67 (1965) (four articles); Kampter et al., Acetylene from Naphtha Pyrolysis, *Chem. Eng.* **73** (5) 80 and 93 (1966) (flowchart and operating costs of high-temperature cracking).

<sup>36</sup>*Hydrocarbon Process.* **58** (4) 99-170 (1979).



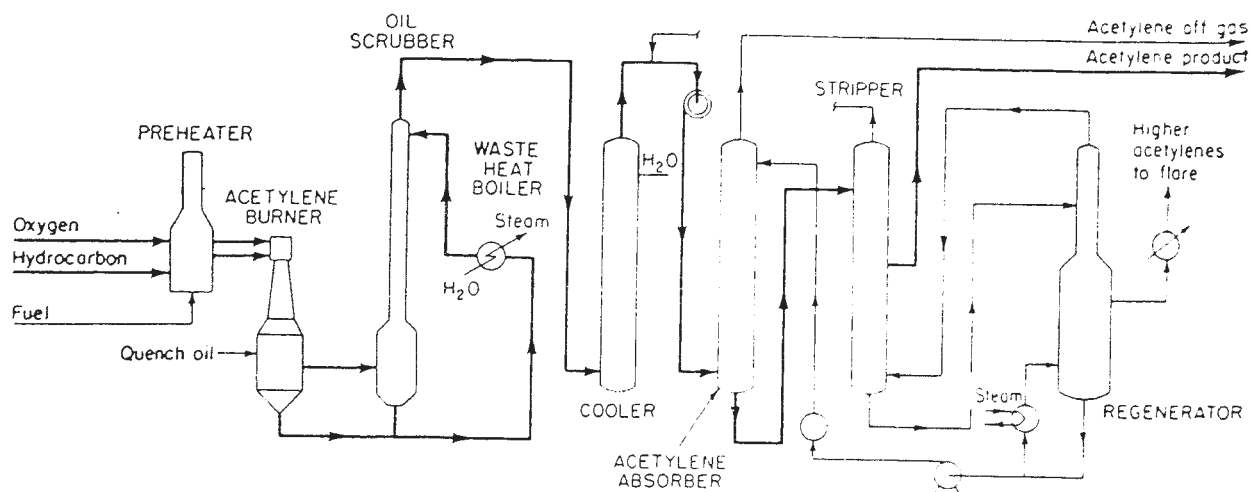


Fig. 4.9. Flowchart for acetylene by partial oxidation from hydrocarbon feedstock (*Chemical Construction Co.*)

Overall reaction of the methane (combustion and splitting) is 90 to 95%, whereas the oxygen is 100 percent converted. Residence time is 0.001 to 0.01 s. The acetylene and gases are cooled rapidly by quench oil or water sprays to 38°C and have the following typical composition, in percent:

Acetylene	8.5	Methane	4
Hydrogen	57	Higher acetylenes	0.5
Carbon monoxide	25.3	Inerts	1.0
Carbon dioxide	3.7	Total	100

The soot is removed in a carbon filter.

The clean gases are compressed to 1.14 MPa.

Acetylene is removed in a column (packed) by a selective solvent, e.g., dimethylformamide. Carbon dioxide is flashed and stripped overhead out of the rich solvent in a column (packed), where the acetylene is fractionated out, giving a 99%+ product with a 30 to 36 percent yield from the carbon in the natural gas.

Higher acetylenes and water are stripped out under reduced pressure, and the solvent is reused.

The Wulff process<sup>37</sup> for acetylene production used an arc furnace to pyrolyze hydrocarbons to acetylene. It has proved to be too expensive to compete now that energy costs have increased so much. It is described in CPI, 4th ed

Acetylene is also recovered from ethylene feedstock prior to ethylene polymerization.<sup>38</sup>

<sup>37</sup>McGraw-Hill Encyclopedia of Science and Technology, vol. 13, McGraw-Hill, New York, 1977, p. 270.

<sup>38</sup>Lorber, Reimann, and Rottmayr, Acetylene Recovered from Ethylene Feedstock, *Chem Eng.* 78 (17) 83 (1971).

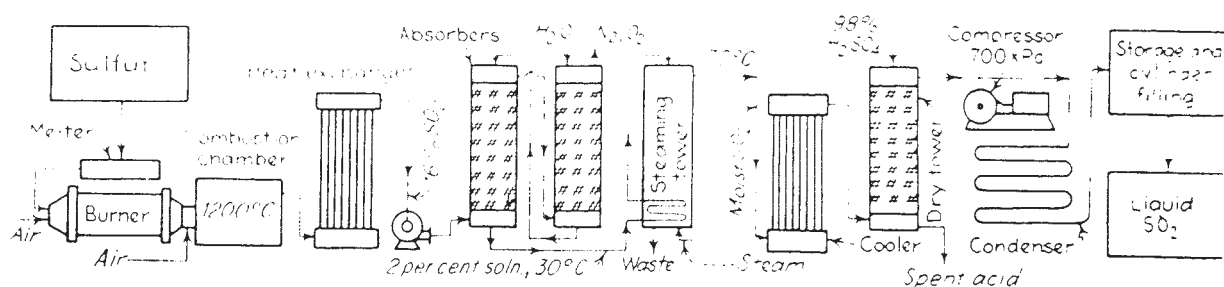


## SULFUR DIOXIDE<sup>39</sup>

Sulfur dioxide may be produced by the burning of sulfur or by the roasting of metal sulfides in special equipment. It may also be obtained by recovery from the waste gases of other reactions. Its production and the subsequent compression and cooling to form liquid sulfur dioxide, which boils at  $-10^{\circ}\text{C}$ , are shown in Fig. 4.10. With very careful control of the amount of air entering the combustion chamber, sulfur dioxide can be produced up to 18% by volume at a temperature of  $1200^{\circ}\text{C}$ . As the gases from the combustion chamber pass through the heat exchanger, they heat the water for the boilers. The cooled gases, containing from 16 to 18% sulfur dioxide, are pumped into the absorbers through acidproof pumps. The strength of the solution from the absorbers is dependent upon the temperature and the strength of the gases entering, but the concentration usually runs about 1.3% with the temperature close to  $30^{\circ}\text{C}$ . A very small amount of sulfur dioxide is lost in the exhaust from the second absorber—about 0.02%. The temperature of the vapors coming from the steaming tower depends upon its design, but usually runs about  $70^{\circ}\text{C}$ . The vapors are cooled and passed through a drying tower in which 98% sulfuric acid is used. Other drying agents may be employed, and some plants by special procedure eliminate the use of this sulfuric acid dryer altogether. The sulfur dioxide is liquefied by compression to about 710 kPa and cooling. It is stored or put into cylinders.

Sulfur dioxide is shipped as a liquid under 200 to 300 kPa pressure. It is obtainable in steel cylinders of from 22- to 45-kg capacity, in 1-t tanks, or in 15-t tank cars. Its uses are numerous. A quite pure commercial grade, containing not more than 0.05% moisture, is suitable for most applications. A very pure grade, however, containing less than 50 ppm of moisture, is supplied for refrigeration. Sulfur dioxide also serves as raw material for the production of sulfuric acid. It finds application as a bleaching agent in the textile and food industries. Following the use of chlorine in waterworks and in textile mills, sulfur dioxide is an effective antichlor for removing excess chlorine. It is an effective disinfectant and is employed as such for wooden

<sup>39</sup>Yaws, Li and Kuo, Sulfur Oxides, *Chem. Eng.* 81 (14) 85 (1974); Potter and Craig, Commercial Experience with an  $\text{SO}_2$  Recovery Process, *Chem. Eng. Prog.* 68 (8) 53 (1972); Profit in Stack Gas, *Chem. Week* 103 (3) 53 (1968).



In order to produce 100 kg liquid  $\text{SO}_2$ , the following materials and utilities are required.

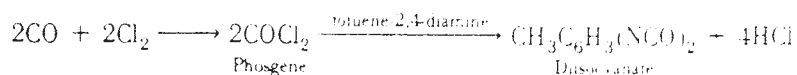
Sulfur	54 kg	Electricity	1.5 MJ
$\text{H}_2\text{SO}_4$ (98%)	30 kg	Steam	340 kg
Water	7500 L	Direct labor	1.1 work-h

Fig. 4.10. Flowchart for liquid sulfur dioxide production.

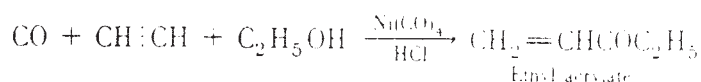
kegs and barrels and brewery apparatus and for the prevention of mold in the drying of fruits. Sulfur dioxide efficiently controls fermentation in the making of wine. It is used in the sulfite process for paper pulp, as a liquid solvent in petroleum refining, and as a raw material in many plants, e.g., in place of purchased sulfites, bisulfites, or hydrosulfites.

## CARBON MONOXIDE

Carbon monoxide is one of the chief constituents of synthesis gas. It is obtained in pure form through cryogenic procedures, with hydrogen as a coproduct. It is an important raw material in the production of methanol and other alcohols and of hydrocarbons. It is a powerful poison. It is used for making diisocyanate and ethyl acrylate by the following reactions:



(1)



## NITROUS OXIDE

Nitrous oxide is generally prepared by heating very pure ammonium nitrate to 200°C in aluminum retorts.



The purification consists of treatment with caustic to remove nitric acid and with dichromate to remove nitric oxide. It is shipped in steel cylinders as a liquid at a pressure of 10 MPa. It is used as an anesthetic, usually mixed with oxygen.

## SELECTED REFERENCES

- Anon.: *Hydrogen, Engineering Design Data*, NBS Monograph 168, Natl. Bur. Standards, 1962.  
 Adler, L. B. and H. B. Shuey: *Acetylene Handling*, AIChE, New York, 1963.  
 Clarke, T. G.: "Helium" in *Minerals Handbook*, U.S. Bureau of Mines, 1977.  
*Cryotech 1973 Proceedings: The Production and Use of Industrial Gases*, IPC, Science and Technology Press, London, 1974.  
 Falbe, J.: *Carbon Monoxide in Organic Synthesis*, Springer-Verlag, New York, 1970.  
 Foh and coworkers: Paper presented at IGT Symposium "Hydrogen for Energy Distribution," July, 1978.  
 Hardie, D.: *Acetylene, Manufacture and Uses*, Oxford, New York, 1965.  
 Kohl, A. L. and F. C. Riesenfeld: *Gas Purification*, 2d ed., Gulf, Houston, 1974.  
 Kropschot, R. H., B. W. Birmingham, and D. B. Mann: *Technology of Liquid Helium*, Natl. Bur. Standards Monograph 111, 1968.  
 McClintock, M.: *Cryogenics*, Reinhold, New York, 1964.

- Meyer, B.: *Sulfur, Energy and Environment*, Elsevier, New York, 1977.
- Miller, S. A.: *Acetylene: Its Properties, Manufacture and Uses*, Academic, New York, 1967, 3 vols.
- Raghurman, K. S. and T. Johansen: The Role of Hydrogen in Chemical, Petrochemical and Petroleum Industries, *KII Newsletter*, April 1975.
- Rylander, P. N.: *Organic Synthesis with Noble Metal Catalysts*, Academic, New York, 1973.
- Stowasser, W.: "Oxygen" in *Mineral Facts and Problems*, U.S. Bureau of Mines Bull. 667, 1980.
- Webber, L. A.: *Thermodynamic and Related Properties of Oxygen*, NASA Ref. Pub. 1101, Natl. Bur. Standards, Dec. 1977.