NOBLE GASES

1. Introduction

The noble gases are helium [7440-59-7], He; neon [7440-01-9], Ne; argon [7440-37-1], Ar; krypton [7439-90-9], Kr; xenon [7440-63-3], Xe; and radon [14859-67-7], Rn. These are all members of Group 18 (VIIIA) of the Periodic Table and are characterized by completely filled valence electron shells. Historically, they have been called the rare or inert gases. But although comparatively rare, krypton, xenon, and radon are not completely inert and exhibit reactivity under certain conditions; all three form stable molecules with highly electronegative elements such as F, Cl, and O. Although inert enough, helium and argon are not rare in terms of available quantities; both are bulk items of commerce. Since commercial quantities of helium are produced from helium-bearing natural gas reserves, at some future time, if those reserves become depleted, helium could once again return to being a truly rare gas.

The noble gases were not isolated until the last decade of the nineteenth century making them the most recently discovered group of stable elements (1–3). While seeking more accurate density values for certain gases during the period 1882–1894, Rayleigh noted that the density of nitrogen isolated by removing oxygen from air was consistently about one-half percent greater than that of nitrogen obtained from chemical reactions. Working with Rayleigh, Ramsay treated atmospheric nitrogen with hot magnesium and obtained a residual gas, $\sim$1.25% of the nitrogen, that was completely unreactive. The gas had a relative density of 19.075 ($O = 16$) and exhibited spectral lines not seen before. In 1894, the discovery of an inert gas was announced by Ramsey and Rayleigh and they called it argon from the Greek *argos*, inactive.

In 1868, within a decade of the development of the spectroscope, an orange-yellow line was observed in the sun's chromosphere that did not exactly coincide with the D-lines of sodium. This line was attributed to a new element which was named helium, from the Greek *helios*, the sun. In 1891, an inert gas isolated from the mineral uranite showed unusual spectral lines. In 1895, a similar gas was found in cleveite, another uranium mineral. This prominent yellow spectral line was then identified as that of helium, which to that time had been thought to exist only on the sun. In 1905, it was found that natural gas from a well near Dexter, Kansas, contained nearly 2% helium (see GAS, NATURAL).

The existence of neon (Greek *neos*, new) was predicted, as was the existence of heavier members of the group. In 1898 krypton (Greek *kryptos*, hidden) was discovered by spectroscopic examination of the residue from a sample of liquid air. Neon was discovered in the same year. A month later, xenon (Greek *xenos*, strange) was isolated from the residue left after distillation of krypton.

Radon-220 [22481-48-7], ^{220}Rn, a decay product of thorium, was discovered by Owens and Rutherford in 1900. The more common radon-222, a decay product of radium, was discovered later in the same year and was isolated in 1902.

Helium-3 [14762-55-1], ^{3}He, has been known as a stable isotope since the middle-1930s and it was suspected that its properties were markedly different from the common isotope, helium-4. The development of nuclear fusion devices in the 1950s yielded workable quantities of pure helium-3 as a decay product from the large tritium inventory implicit in maintaining an arsenal of fusion weapons (see DEUTERIUM AND TRITIUM) Helium-3 is one of the very few stable materials where the only practical source is nuclear transmutation. The chronology of the isolation of the other stable isotopes of the noble gases has been summarized (4).

2. Occurrence

Helium, plentiful in the cosmos, is a product of the nuclear fusion reactions that are the prime source of stellar energy. The other members of the noble gases are thought to have been created like other heavier elements by further nuclear condensation reactions occurring at the extreme temperatures and densities found deep within stars and in supernovas.

On earth, the only practical sources of the stable noble gases are the atmosphere and certain helium-bearing natural gases. Faint concentrations of helium and argon are occluded in some minerals. The neon, krypton, xenon, and most of the argon isotopes were likely part of the original mass that condensed to form the earth. However, the earth's gravitational field is inadequate to prevent helium's escape from the atmosphere. Helium is being formed continuously on earth by α-decay of heavier elements such as uranium and thorium, the α-particle being simply a fully ionized helium atom. Thus, the atmospheric helium concentration represents a dynamic equilibrium between the gain of helium diffusing from the earth's crust and the loss of helium into space. The total terrestrial inventory of helium is estimated to be $4.9 \times 10^{14}\,m^3$, where the volume is measured throughout at 101.3 kPa (1 atm) absolute pressure and 15°C (5).

Argon-40 [7440-37-1] is created by the decay of potassium-40. The various isotopes of radon, all having short half-lives, are formed by the radioactive decay of radium, actinium, and thorium. Krypton and xenon are products of uranium and plutonium fission, and appreciable quantities of both are evolved during the reprocessing of spent fuel elements from nuclear reactors (qv).

Table 1. **Components of Dry Air**

Gas	Concentration,[a] μL/L	Minimum work of separation at 300 K, kJ/mol[b]	Normal boiling point, K
	Principal constituents		
nitrogen	$780,840 \pm 40$	1.68	77.35
oxygen	$209,460 \pm 20$	6.11	90.19
argon	$9,340 \pm 10$	14.14	87.28
carbon dioxide	300 ± 30	22.73	194.67[c]
neon	18.21 ± 0.04	29.72	27.09
helium-4	5.24 ± 0.05	32.82	4.22
krypton	1.14 ± 0.01	36.63	119.80
hydrogen	ca 0.05	38.68	20.27
xenon	0.087 ± 0.001	43.04	165.03
	Variable impurities		
methane	1.7[d]		111.66
carbon monoxide	<1		81.70
sulfur dioxide	1		263.2
nitrogen dioxide	0.5		294.2
ozone	<0.1		161.8
nitrous oxide	<0.02		184.68
radon	6×10^{-14}		211

[a] Ref. 6.
[b] To convert J to cal, divide by 4.184.
[c] Sublimation temperature.
[d] Ref. 7.

In the composition of dry air (Table 1), nine principal constituents are constant wherever free air is sampled. Five of these are the stable noble gases. Other trace impurities in air vary in concentration from place to place; among these is radon. The longest lived isotope, ^{222}Rn, has a half-life of 3.825 days, which is short compared to the atmosphere's mixing time. The concentrations of several of the variable impurities are comparable to that of krypton and an order of magnitude greater than that of xenon. Also listed in Table 1 is the thermodynamic minimum work for isobaric, isothermal separation per mole of each component from air at 300 K (8). Practical separations most often involve cryogenic condensations and distillations, thus the normal boiling point of each component is also listed (see CRYOGENIC TECHNOLOGY; NITROGEN; OXYGEN).

The principal source of helium is certain natural gas fields. The helium contents of >10,000 natural gases in various parts of the world have been measured. Helium concentrations of a few are listed in Table 2. In the United States, recovery of helium is economical only for helium-rich gases containing more than ~0.3 vol% helium. Most of the United States helium resources are located in the midcontinent and Rocky Mountain regions, and ~89% of the known United States supply is in the Hugoton field in Kansas, Oklahoma, and Texas; the Keyes field in Oklahoma; the Panhandle and Cliffside fields in Texas; and the Riley Ridge area in Wyoming.

Table 2. **Helium Concentrations of Helium-Bearing Natural Gases**^{a}

Location	Field site	Concentration, vol%
United States		
Wyoming	Tip Top Field	0.4–0.8
San Juan, New Mexico	Beautiful Mountain	4.05
North Slope, Alaska	South Barroweast	2.54
Young, Texas	Young Regular	1.17
Grant, Kansas	Hugoton (Comprstation)	0.44
Canada		
Alberta	Worsley	0.53
Ontario	Norfolk	0.36
the Netherlands	Groningen	0.05
	DeWijk	0.05
Poland	Ostrow	0.4
North Sea, British sector	Indefatigable	0.05
West Germany, Niedersachsen	Apeldorn	0.12
CIS	Urengoi	0.055
	Orenburg	
Orange Free State	O.F.S. Goldfields	2.91
Algeria	Hassi R'Mel	0.19
Australia, North Territory	Palm Valley	0.21

^{a} Ref. 10.

2.1. Resources and Conservation.

The availability of the noble gases from the atmosphere is unlikely to change. There are no environmental sinks for these practically inert materials, and quantities removed from the atmosphere are eventually returned.

Upon the United States entry into World War I in 1917, helium became a war material of first priority. Helium was sought to replace hydrogen as the lifting gas in lighter than air craft for military use. As a war material, helium became a government monopoly, was given a code name, and was shrouded in secrecy. By the war's end, quantities of helium had been produced, but none had reached combat.

In 1925, the first *Helium Conservation Act* made the U.S. Bureau of Mines responsible for all helium activities including the construction and operation of helium-separation plants, planning, and experimental work. Sales of helium to nongovernmental users were prohibited until 1937. Helium facilities were, therefore, in place at the beginning of World War II, and helium's availability as a lifting gas proved to be of great value in the antisubmarine campaigns. Following World War II, new technologies demanded ever-increasing amounts of helium. By the end of the 1950s, demand exceeded production capabilities of the Bureau of Mines' plants, and depletion of resources came into question (11).

In a move to conserve the helium being wasted in natural gas combustion, the 1960 *Helium Act Amendments* allowed the government to enter long-term contracts for the purchase of crude helium recovered by private companies and to store the crude helium. The program was to be supported by an increase in the price of the purified helium by the Bureau of Mines. Over the next decade, however, helium usage increased more slowly than had been projected, reserves accumulated more rapidly than had been anticipated, and private producers took an increasing share of the market by selling pure helium at prices far below federal prices (12). Thus in 1971 the government canceled the entire helium conservation program. In the mid-1970s, the Bureau of Mines began accepting privately owned crude helium for storage in the Cliffside gasfield under long-term contracts.

Between mid-1970s and mid-1990s, the private helium industry continued to develop and significant investments were made in modern production plants, distribution equipment and infrastructure. The helium refining facilities being operated by the U.S. government had come to be viewed as outdated, costly to operate and maintain and no longer essential in supplying pure helium to government users and private industry. On October 9, 1996, *The Helium Privatization Act of 1996 (P.L. 104-273)* was signed into law by President Clinton. The purpose of the Act was to (*1*) terminate the federal government's production and sale of Grade A helium (ie, minimum of 99.995% helium), (*2*) dispose of the government's refining and sales related assets, and (*3*) sell off all of the crude helium (in excess of 0.6 bilion cubic feet) contained in the Federal Helium Reserve stored in the Cliffside gasfield. By doing so, the accumulated debt of the Federal Helium Program (~$1.4 billion) would be repaid to the U.S. treasury. This was to be accomplished by the year 2015 and was to be done in a manner that would not be disruptive to private industry. By January 1, 2005, the Secretary of the Interior was to commence offering for sale, on a straight-line basis, the ~865 million m^3 (30.5 billion ft^3) of government-owned crude helium contained in the Federal Reserve. The first annual sale of crude helium from the government stockpile was held in October of 2003 by the U.S. Bureau of Land Management. As of September 30, 2004, the quantity of crude helium remaining in the Federal Reserve was ~765 million m^3 (27 billion ft^3) (13).

Helium continues to be an important material, but its significance has shifted from a simple lifting gas to a unique medium essential to high technology. The cost of separation from fuel gases and of long-term storage of crude helium is great, yet the cost of satisfying all helium requirements by extraction from the atmosphere is assuredly even higher. Estimates in 1994 (14) of the total U.S. helium reserves were $\sim 12.2 \times 10^9\,m^3$.

3. Physical Properties

3.1. Pure Elements. All of the helium-group elements are colorless, odorless, and tasteless gases at ambient temperature and atmospheric pressure. Chemically, they are nearly inert. A few stable chemical compounds are formed by radon, xenon, and krypton, but none has been reported for neon and helium. The helium-group elements are monoatomic and are considered to have perfect atomic spherical symmetry. Because of the theoretical interest generated by this atomic simplicity, the physical properties of all the helium-group elements except radon have been well studied.

Some of the physical properties of the helium-group elements are summarized in Table 3. The values are those for the naturally occurring isotopic mixtures

Table 3. **Physical Properties of the Helium-Group Elements**

Property	^{3}He	^{4}He	Ne	Ar	Kr	Xe	Rn	References
atomic number	2	2	10	18	36	54	86	
atomic weight	3.0160	4.0026	20.183	39.948	83.80	131.30	222	15–17
critical point								
temperature, K	3.324	5.2014	44.40	150.86	209.4	289.74	378	18–23
pressure, kPa,[a]	116.4	227.5	2654	4898	5502	5840	6280	18–23
density, kg/m^3	41.3	69.64	483	535.7	908	1100		15,19–23
normal bp, K	3.1905	4.224	27.102	87.28	119.79	165.2	211	18,19,21–25
triple point (tp)								
temperature, K			24.562	83.80	115.76	161.37	202	20,22,24–26
pressure, kPa[a]			43.37	68.90	73.15	81.66	70[b]	20,24–26
density, kg/m^3 gas at 101.3 kPa,[a] 0°C	0.1347	0.17850	0.9000	1.7838	3.7493	5.8971	9.73	22,27
gas, normal bp	23.64	16.89	9.552	5.767	8.6	11		19–22,28
liquid, normal bp	58.9	125.0	1207	1393.9	2415	3057	4400	15,19,21,22,25,29
liquid, tp			1247	1415	2451	3084		20,21,24,25
solid, tp			1444	1623	2826	3540		22,30,31
gas/liquid volume ratio[c]	437.4	700	1340	781	644	518	452	15,22
heat of vaporization, normal bp, J/mol[d]	25.48	81.70	1741	6469	9012	12,640	18,100	15,17,19,21,22, 24,25
heat of fusion, tp, J/mol[d]			335	1183	1640	2313	3247	17,22
heat capacity, C_p, gas at 101.32 kPa,[a]	20.78	20.78	20.79	20.85	20.95	21.01	21[b]	19,21,27,32,33
25°C, J/(mol K)[d] C_s, saturated liquid, normal bp, J/(mol K)[d]	16.74	18.12	37.24	45.6	44.9	44.56		20,22,29,34–36
sonic velocity, gas at 101.32 kPa,[a] 0°C, m/s	1122[b]	973	433	307.8	213	168		19,22,35,37
thermal conductivity, mW/(m K) gas, 101.32 kPa,[a] 0°C	163.6[b]	141.84	46.07	16.94	8.74	5.06		22,38,39

liquid, normal bp	21.3	31.4	129.7	121.3	88.3	73.2		15,22,40
viscosity								
gas, 101.32 kPa,[a] 25°C, Pa s	17.2[b]	19.85	31.73	22.64	25.3	23.1	23.3	22,40
liquid, normal bp mPa s (=cP)	0.00161	0.0030	0.124	0.275	0.431	0.528		22,41–43
solubility in water, 20°C, mL/kg[c]		8.61	10.5	33.6	59.4	108.1	230	22
first ionization potential, eV		24.586	21.563	15.759	13.999	12.129	10.747	44
minimum excitation energy, eV		19.818	16.618	11.548	9.915	8.315	6.772	44
stable isotopic abundance, atomic %	1.3×10^{-4}[f] 1.7×10^{-5}[g]	100	N^{20}e=90.5 N^{21}e=0.27 N^{22}e=9.23	A^{36}r=0.337 A^{38}r=0.063 A^{40}r=99.60	K^{36}r=0.35 K^{80}r=2.27 K^{82}r=11.56 K^{83}r=11.55 K^{84}r=56.90 K^{86}r=17.37	X^{124}e=0.096 X^{126}e=0.090 X^{128}e=1.92 X^{129}e=26.44 X^{131}e=4.08 X^{131}e=21.18 X^{132}e=26.89 X^{134}e=10.44 X^{136}e=8.87	no stable isotopes	4

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[a] To convert kPa to psi, multiply by 0.145.

[b] Estimated.

[c] Volume of gas at 101.32 kPa and 0°C equivalent to unit volume of liquid at normal bp.

[d] To convert J to cal, divide by 4.184.

[e] mL (101.32 kPa, 0°C) dissolved per kg water having partial pressure of pertinent gas of 101.32 kPa.

[f] In the atmosphere.

[g] In wells.

of each element except for helium which has separate ^{3}He and ^{4}He entries. These two stable helium isotopes exhibit large differences in many of their physical properties. Extensive reviews of physical properties are available (22,45–47). Detailed thermodynamic property correlations and tables have been published for helium (19,48,49), neon (20,49), and argon (19,21,49). Tabulations of the unstable isotopes of the helium-group elements and the corresponding decay modes are given in Ref. 50 and 51.

Radon is the heaviest of the helium-group elements and the heaviest of the normal gaseous elements. It is strongly radioactive. The most common isotope, ^{222}Rn, has a half-life of 3.825 days (50). Radon's scarcity and radioactivity have severely limited the examination of its physical properties, and the values given in Table 3 are much more uncertain than are the values listed for the other elements.

The physical properties of argon, krypton, and xenon are frequently selected as standard substances to which the properties of other substances are compared. Examples are the dipole moments, nonspherical shapes, quantum mechanical effects, etc. The principle of corresponding states asserts that the reduced properties of all substances are similar. The reduced properties are dimensionless ratios, such as the ratio of a material's temperature to its critical temperature, density to critical density, pressure to critical pressure, etc. The classical, two-parameter law of corresponding states requires that if pure materials are compared at conditions where two of the reduced properties are identical, then the values of any third reduced property also will be identical. Argon, krypton, xenon, and presumably radon all obey the two-parameter law of corresponding states particularly well, a fact that is a further indication of their normal behavior.

Except for helium, all of the elements in Group 18 (VIIIA) freeze into a face-centered cubic (fcc) crystal structure at normal pressure. Both helium isotopes assume this structure only at high pressures. The formation of a high pressure phase of solid xenon having electrical conductivity comparable to a metal has been reported at 33 GPa (330 kbar) and 32 K, and similar transformations by a band-overlap process have been predicted at 15 GPa (150 kbar) for radon and at 60 GPa (600 kbar) for krypton (52).

3.2. Quantum Mechanical Effects.

The very light gases show significant deviations from the classical law of corresponding states, especially at cryogenic temperatures. This anomalous behavior is caused by quantum mechanical effects that become increasingly significant with decreasing atomic weight. Only small quantitative effects can be observed in neon's properties; the effects in hydrogen are somewhat more pronounced; but these quantum mechanical effects have profound qualitative effects on the behavior of helium at low temperature. The liquid and solid phases of the two helium isotopes exhibit physical characteristics found in no other substances.

3.3. Solid Phases.

Quantum mechanical descriptions of solids do not allow the complete cessation of molecular motion even at absolute zero. Instead, a certain zero-point motion about the molecule's average position in the crystal lattice is required. The magnitude of this motion increases both with decreasing molecular weight and with decreasing van der Waal's attraction. The helium isotopes have the largest zero-point motion of any substance. This is manifested

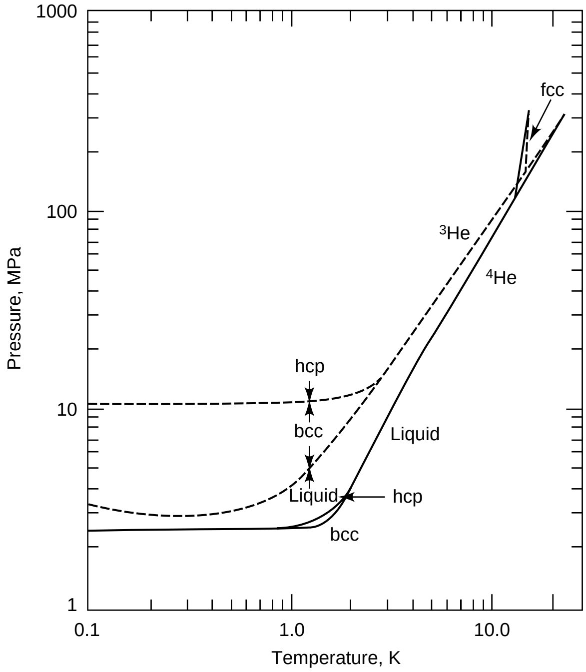

Fig. 1. Solid–liquid phase diagram for (—) ^{3}He and (—) ^{4}He, where bcc = body-centered cubic, fcc = face-centered cubic, and hcp = hexagonal close-packed (54). To convert MPa to psi, multiply by 145.

in several unique characteristics of condensed helium (53). The helium isotopes are the only known substances that do not freeze under their own vapor pressure. All other materials have a triple point with unique temperature and pressure at which the solid, liquid, and vapor phases coexist. Neither helium-3 nor-4 has a triple point. Under moderate pressure, both remain liquid to absolute zero.

Even at the lowest temperatures, a substantial pressure is required to solidify helium, and then the solid formed is one of the softest, most compressible known. The fluid–solid phase diagrams for both helium-3 and-4 are shown in Fig. 1 (54). Both isotopes have three allotropic solid forms: an fcc structure at high pressures, an hcp structure at medium and low pressures, and a bcc structure over a narrow, low pressure range for helium-4, and over a somewhat larger range for helium-3. The melting pressure of helium-4 has been measured up to 24°C, where it is 11.5 GPa (115 kbar) (55).

The melting curves of both helium isotopes show a minimum. For helium-4, the minimum is at 2.53 MPa (25 atm) and 0.775 K (56) but the minimum is very shallow, only ∼0.7 kPa (0.1 psi) below the melting pressure at absolute zero. The minimum in the helium-3 melting curve, 0.32 K and 2.93 MPa (425 psia) (57), is much more distinct. It was predicted (58) from quantum mechanical arguments that at very low temperatures the entropy of liquid helium-3 should be less than that of the solid; hence, the melting curve slope should be negative, and the heat of solidification should also be negative. This is indeed the case, and adiabatic compression refrigerators based on the Pomeranchuk effect are used to produce temperatures in the millikelvin (mK or 0.001 K) range (see also REFRIGERATION).

3.4. Liquid Helium-4. Quantum mechanics defines two fundamentally different types of particles: bosons, which have no unpaired quantum spins, and fermions, which do have unpaired spins. Bosons are governed by Bose-Einstein statistics which, at sufficiently low temperatures, allow the particles to collect into a low energy quantum level, the so-called Bose-Einstein condensation. Fermions, which include electrons, protons, and neutrons, are governed by Fermi-Dirac statistics which forbid any two particles to occupy exactly the same quantum state and thus forbid any analogue of Bose-Einstein condensation. Atoms may be thought of as assemblies of fermions only, but can behave as either fermions or bosons. If the total number of electrons, protons, and neutrons is odd, the atom is a fermion; if it is even, the atom is a boson.

Because the helium-4 atom contains an even number of fermions, it is a boson. When saturated liquid helium is cooled <2.175 K, it undergoes what is generally recognized as the manifestation of a Bose-Einstein condensation (59). The liquid displays a striking and unique change of properties; it becomes a superfluid. A phase diagram for helium-4 is shown in Fig. 2. Normal liquid helium-4 is termed helium I, and the superfluid liquid, helium II. The transition temperature varies with pressure from 2.172 K and 5.04 kPa (0.7304 psia) for the

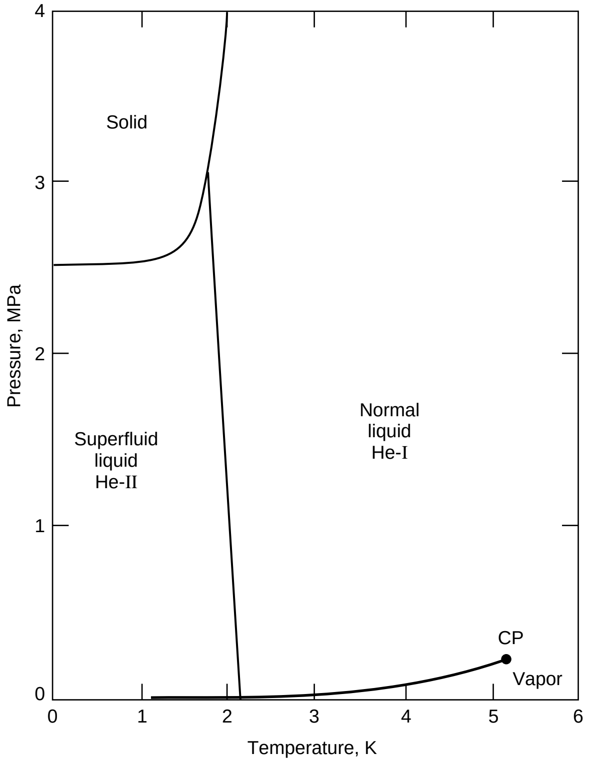

Fig. 2. Phase diagram for helium-4, where CP is the critical point. To convert MPa to psi, multiply by 145.

saturated liquid to 1.763 K and 3.01 MPa (437 psia) at the melting point (19,60). The superfluid transition is not first order; there is no heat of transition as such. Instead, the heat capacity of liquid helium-4 shows a sharp peak at the transition temperature. Because the peak somewhat resembles the lower case Greek letter lambda, the superfluid transition point is often called the lambda point of helium-4. The transition to the superfluid state can be clearly seen in experiments in which the temperature of a liquid helium-4 bath is reduced by continuously pumping away the helium vapors above the liquid. As the helium vapor pressure is reduced, the liquid boils vigorously until the transition temperature is reached. The liquid then abruptly becomes completely quiescent, although evolution of helium vapor from the liquid surface continues unabated.

In many ways, helium II behaves as a liquid having a vanishingly small viscosity and a very high thermal conductivity. Detailed explanations of these properties involve complex quantum mechanical analyses (56,61,62). However, at least a phenomenological description of many of the characteristics of helium II can be gained from a two-fluid model. This model postulates that helium II is a mixture of two interpenetrating liquid components, one being similar to helium I, a reasonably normal liquid, and the other being a perfect superfluid, the concentration of the perfect zero to 0% at the lambda point. The converse is also assumed, namely, that any increase in superfluid concentration must be accompanied by a reduction in temperature.

There is assumed to be no interaction between the superfluid and normal components, thus the superfluid component can diffuse very rapidly to a heat source where it absorbs energy by reverting to the normal state. It thereby produces the very high effective thermal conductivity observed in helium II.

The viscosity of a liquid can be determined either from its rate of isothermal flow through a capillary or from the hydrodynamic drag it exerts on a rotating disk or cylinder (see RHEOLOGY AND RHEOLOGICAL MEASUREMENTS). Provided that the flow rate through the capillary is not too fast, such a determination indicates a vanishingly small viscosity for helium II. Viscosities of helium II determined from hydrodynamic drag experiments, however, have reasonable and finite values. The explanation based on the two-fluid model is that only the superfluid component flows through the capillary and that the normal component in the bulk liquid helium II surrounding a rotating cylinder produces the hydrodynamic drag.

When the superfluid component flows through a capillary connecting two reservoirs, the concentration of the superfluid component in the source reservoir decreases, and that in the receiving reservoir increases. When both reservoirs are thermally isolated, the temperature of the source reservoir increases and that of the receiving reservoir decreases. This behavior is consistent with the postulated relationship between superfluid component concentration and temperature. The converse effect, which may be thought of as the osmotic pressure of the superfluid component, also exists. If a reservoir of helium II held at constant temperature is connected by a fine capillary to another reservoir held at a higher temperature, the helium II flows from the cooler reservoir to the warmer one. A popular demonstration of this effect is the fountain experiment (56).

Superfluid helium can pass easily through openings so small that they cannot be detected by conventional leak detection methods. Such leaks, permeable only to helium II, are called superleaks. They can be a source of frustrating difficulties in the construction of apparatus for use with helium II.

Another unique phenomenon exhibited by liquid helium II is the Rollin film (63). All surfaces below the lambda point temperature that are connected to a helium II bath are covered with a very thin (several hundredths μm) mobile film of helium II. For example, if a container is dipped into a helium II bath, filled, and then raised above the bath, a film of liquid helium flows up the inner wall of the container, over the lip, down the outer wall, and drips from the bottom of the suspended container back into the helium II bath. Similarly, if the empty container is partially submerged in the helium II bath with its lip above the surface, the helium film flows up the outer wall of the container, over its lip, and into the container. This process continues until the level of liquid in the partially submerged container reaches that of the helium II bath.

Several oscillatory phenomena occur in helium II. Ordinary sound waves are propagated in a normal manner in helium II. To distinguish ordinary sound from the other wave-like phenomena, it is called first sound. In first sound, the superfluid and normal components oscillate exactly in phase, thus producing the density wave associated with normal sound. When the superfluid and normal components oscillate exactly out of phase, there is no periodic change in bulk liquid density, but there is a periodic change in the concentration of the superfluid component. This concentration difference is observable as a periodic change in temperature. Second sound, then, is a propagation of heat pulses that has all of the characteristics associated with wave propagation, such as reflection, refraction, and interference. Third sound involves a simultaneous thermal and density wave propagation in the Rollin film in which free oscillation of the normal fluid component is inhibited by viscous wall effects. Fourth sound is the transmission of correlated thermal and density waves through densely packed beds of fine powders that effectively immobilize the normal fluid component.

3.5. Liquid Helium-3.

The helium-3 atom contains an odd number of fermions; thus it is itself a fermion. For many years, it was expected that liquid helium-3 might have relatively normal properties at even the lowest temperatures. This expectation was tempered, however, by quasisuperfluid behavior observed in another fermion system. The conduction electrons in metals are fermions, and at low temperatures, some metals become superconducting. Their resistance to direct current becomes identically zero which implies a superfluid behavior of the conduction electrons. In 1957 (64), superconductivity was explained by showing that a net attractive force between pairs of electrons could be created through their interactions with the lattice ions (64). These bound pairs formed a single quasiparticle having an even number of fermions that then behaved as a boson. This theory implied that, at low enough temperature, helium-3 atoms should also form bound pairs and show some form of superfluidity.

In 1971 a helium-3 adiabatic compression refrigerator was used to discover the superfluid transition at temperatures below 0.003 K (65). It was soon found that helium-3 has not one but three superfluid phases, and that these have properties quite different from superfluid helium-4 (66–68). The phases are magnetic, and many of the physical properties are anisotropic. A solid–liquid phase

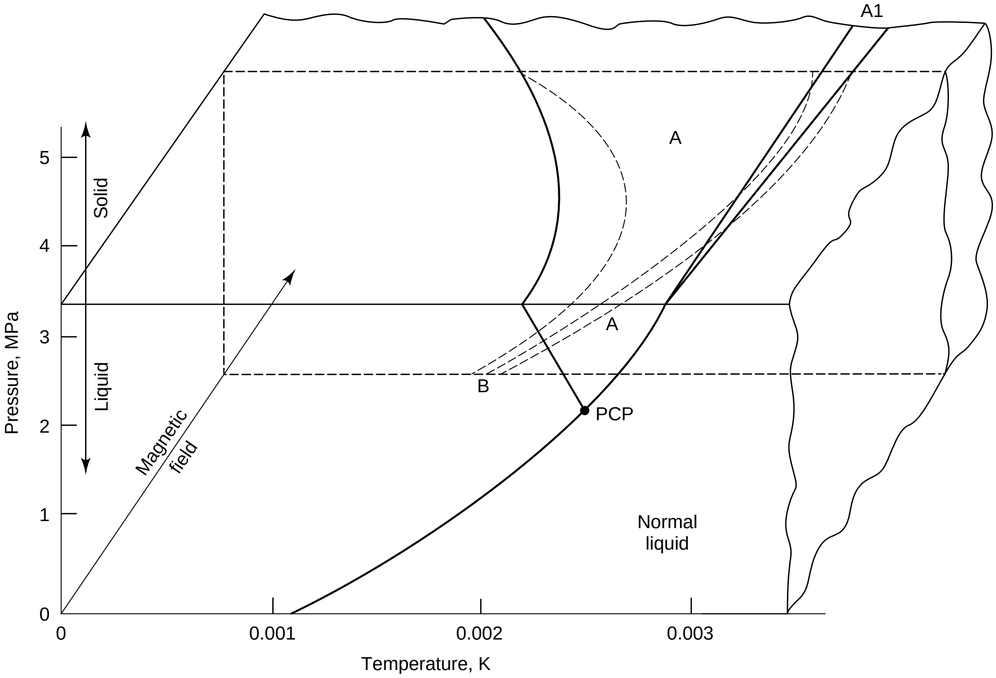

Fig. 3. Phase diagram for helium-3, where A, B, and A1 represent the three superfluid phases and PCP is the polycritical point. The dashed lines indicate the effect of an applied magnetic field. See text. To convert MPa to psi, multiply by 145.

diagram showing the three primary variables of state pressure, temperature, and magnetic field, is given in Fig. 3. In the absence of a magnetic field, only two superfluid phases, A and B, exist; and there is a polycritical point (PCP) at which three liquid phases, A, B, and normal, coexist. As a magnetic field is applied to the liquid, indicated by the dashed plane in Fig. 3, the polycritical point disappears; the A–B transition extends downward in pressure to the saturated liquid line, which is practically zero pressure; and a third superfluid phase, A1, interposes itself between the A and normal phases. A principal distinguishing feature of the three superfluid phases is their distinctive nuclear magnetic resonance characteristics (see MAGNETIC SPIN RESONANCE).

3.6. Mixtures. A number of mixtures of the helium-group elements have been studied and their physical properties are found to show little deviation from ideal solution models. Data for mixtures of the helium-group elements with each other and with other low molecular weight materials are available (69). A similar collection of gas–solid data is also available (70).

The fundamental differences in the quantum mechanical character of the two helium isotopes created much interest in the properties of mixtures. Several reviews are available (71–73). Mixtures of isotopes of a single element usually behave quite ideally, but in the case of ^{3}He–^{4}He solutions, nonideality reaches the point of forming two immiscible liquid phases. The liquid-phase diagram for ^{3}He–^{4}He solutions at low pressure is shown as the solid curves in Fig. 4.

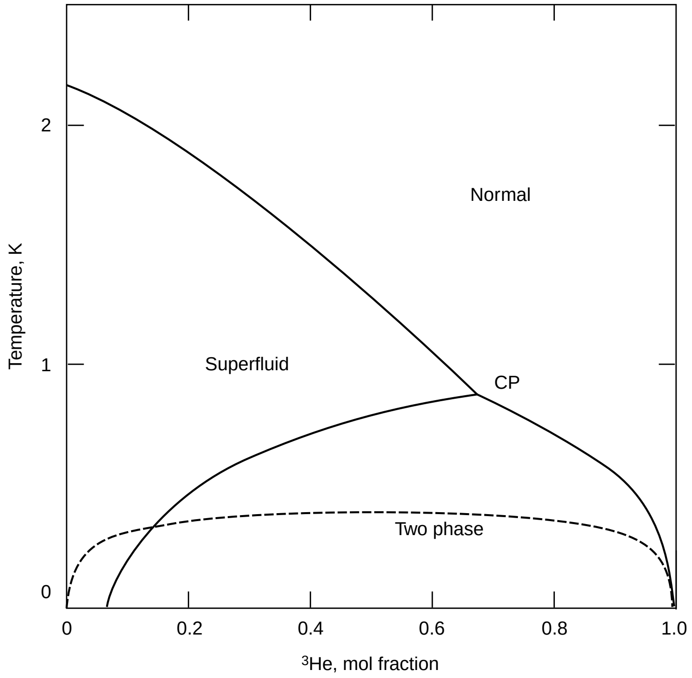

Fig. 4. Phase diagram for liquid and solid mixtures of ^{3}He and ^{4}He where CP is the critical point; (—), liquid; (—), solid.

The solutions undergo the superfluid transition, but the transition temperature is depressed by increases of ^{3}He concentration. Below a solution critical point at 0.867 K and 67.5 mol% ^{3}He (72), two immiscible liquid phases can form. The ^{4}He -rich phase is superfluid and the ^{3}He-rich phase remains normal, at least to >0.003 K. The solubility of ^{4}He in ^{3}He appears to approach zero as the temperature approaches zero, but the solubility of ^{3}He in ^{4}He does not; it remains finite (6.4 mol%) as absolute zero is approached (71).

Below ~0.5 K, the interactions between ^{3}He and ^{4}He in the superfluid liquid phase becomes very small, and in many ways the ^{4}He component behaves as a mechanical vacuum to the diffusional motion of ^{3}He atoms. If ^{3}He is added to the normal phase or removed from the superfluid phase, equilibrium is restored by the transfer of ^{3}He from a concentrated phase to a dilute phase. The effective ^{3}He density is thereby decreased producing a heat-absorbing expansion analogous to the evaporation of ^{3}He. The ^{3}He density in the superfluid phase, and hence its mass-transfer rate, is much greater than that in ^{3}He vapor at these low temperatures. Thus, the pseudoevaporative cooling effect can be sustained at practical rates down to very low temperatures in helium-dilution refrigerators (73).

Unusual behavior has also been observed in solid mixtures of ^{3}He and ^{4}He. In principle, all solid mixtures should separate as absolute zero is approached, but because of kinetic limitations, this equilibrium condition is almost never observed. However, because of high diffusivity resulting from the large zero-point motion in solid helium, this sort of separation takes place in a matter of hours in solid mixtures of ^{3}He and ^{4}He (54,62). The two-phase region for the solid mixture is outlined by the dashed curve in Fig. 4. The two-phase dome is shallow, and its temperature maximum is 0.38 K.

4. Production

Helium is separated from helium-bearing natural gases usually, but not always, in the process of removing nitrogen to improve the fuel value of the gas. Thus, in a sense, the principal part of commercial helium is as a by-product. Argon, neon, krypton, and xenon, as well as small quantities of helium, are obtained from by-product streams that are concentrated during the separation of air to produce oxygen (qv) and nitrogen (qv). Radon is collected as a daughter product of the fission of radium, and helium-3 is the daughter product of tritium.

4.1. Helium from Natural Gas. Recovery of helium from a given natural-gas stream depends almost entirely on the total economic picture of the stream. In the United States, the lowest practical helium level that is recovered is most frequently 0.3 vol%, although helium is sometimes ignored, and hence wasted, in streams containing somewhat higher concentrations. In other parts of the world where political considerations sometimes interact with the economic, the use of helium concentrations <0.3 vol% may be commercially justified. In the production of liquefied natural gas (LNG), helium recovery may be feasible even if the feed stream to the LNG plant has a helium concentration as low as 0.05 vol%. This is due to the fact that (*1*) world-scale LNG production plants typically process extremely large quantities of gas (11–110 million m^3/day) and (*2*) the LNG production process concentrates helium in the plant's nitrogen waste stream (from 3 to 7 vol%).

Natural-gas components include water vapor, carbon dioxide (qv), sometimes hydrogen sulfide, heavier hydrocarbons (qv), methane, nitrogen, small amounts of argon, traces of neon and hydrogen, and helium. The production of pure helium from natural gas requires three basic processing steps (74).

First, is the removal of impurities. Water, carbon dioxide, and sulfides are removed by scrubbing with monoethanolamine and diethylene glycol, followed by drying with alumina. Then the natural gas is concentrated in helium as the higher boiling hydrocarbons are liquefied and collected. Crude helium, concentrated to perhaps 70% and containing nitrogen, argon, neon, and hydrogen, undergoes final purification at pressures up to 18.7 MPa (2700 psi). The crude material is chilled to 77 K in liquid nitrogen-cooled coils of a heat exchanger. Under the high pressure, the low temperature liquefies most of the remaining nitrogen and argon, allowing the helium together with last traces of nitrogen, neon, and hydrogen to separate. Evaporation of nitrogen reduces the temperature and nitrogen content of the helium before it passes into liquid-nitrogen-cooled adsorbers. Activated charcoal operating at liquid nitrogen temperatures or below is capable of adsorbing all nonhelium gases. Hence, passage through these adsorbers yields helium that exceeds 99.9999% in purity. Both concentration and purification steps require nitrogen refrigeration, which is obtained by expansion engines or turbines as well as by expansion valves.

A typical variation of the process suitable for low heating-value gas upgrade would operate with a 5.5 MPa (800 psig) feed followed by Joule-Thomson expansion to 2 MPa (300 psig) and double-column distillation to separate nitrogen from liquid hydrocarbons. This column would also contain a noncondensable gas stream containing helium. This process supplies its own refrigeration and eliminates the need for liquid nitrogen. The need for a 14 MPa (2000 psi) system is also eliminated if product helium is in liquefied form.

Helium may also be separated from natural gas using a pressure swing adsorption (PSA) processes to recover helium at >99.99% purity. This type of process is probably less costly for the production of gaseous helium but might be uneconomical for liquefied helium production. The PSA process is widely used to produce specification pure helium from 85+% crude helium in conjunction with cryogenic enrichment of the ~50% helium raffinate.

4.2. Noble Gases from the Atmosphere. Air contains 0.93% argon, lesser amounts of neon, helium, and krypton, and less of xenon (Table 1). Air is the only practical source in all of these elements except for helium. In the separation of air through a distillation–liquefaction process, the noble gases concentrate either (*1*) as noncondensable gases, ie, helium, neon, plus hydrogen, at liquid nitrogen temperatures; (*2*) as a primary inert, ie, argon, that can reduce oxygen purity up to 5% if not removed; or (*3*) as a trace inert, up to 10 ppm Kr–Xe also in the oxygen product, which may be ignored or removed for its own value (75,76).

4.3. Concentration of Rare Gas Crudes. The distillation of air is classically carried out in the double-column and auxiliary equipment of Fig. 5. Dry, CO_2-free air, chilled to partial liquefaction by heat exchange, is introduced into the lower nitrogen or high pressure column. This unit is typically operated at 620–720 kPa (90–104 psi) pressure. As the air is introduced, partial condensation occurs; the nitrogen vapor distills up the column to become pure N_2 at the top, while the remaining liquid air having lost approximately one-half of the original nitrogen and having as a consequence a higher boiling point, collects at the bottom. Condensation of nitrogen at the top provides the reflux necessary to rectify the gas streaming up as well as pure nitrogen liquid for reflux liquid to be supplied to the upper oxygen (or low pressure) column and product for removal to storage. Note that although the top of the lower (nitrogen) column and the bottom of the upper (oxygen) column are in thermal equilibrium; no gas or liquid can pass directly between them.

Because of their very low boiling points, helium, neon, and hydrogen are noncondensable under the conditions at the top of the nitrogen column, and they concentrate in the nitrogen gas there. Because they cut down on the rate of condensation of nitrogen and thereby reduce the thermal efficiency of the process, they must be withdrawn. The noncondensable stream withdrawn may have a neon, helium, or hydrogen content that varies from 1 to 12% (the balance being nitrogen), depending on plant design, objective of plant operation, and hence rate of withdrawal. For recovery, the noncondensable gases are first concentrated in the neon column shown in Fig. 5, where a significant part of the nitrogen is liquefied and returned. The neon–helium crude is further separated and purified in processing as described below.

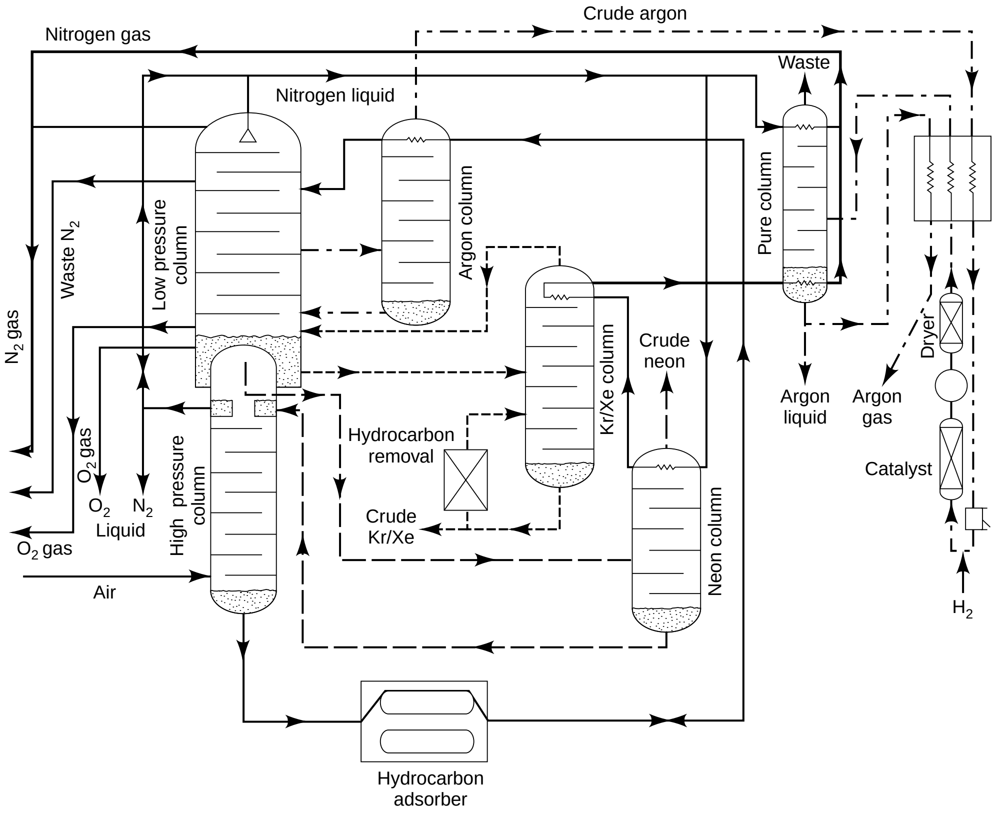

Fig. 5. Production of helium-group gases in a classical air-separation plant.

The oxygen-rich liquid (~40% O_2) that arrives at the bottom of the lower (high pressure) column is transferred by pressure differential to the upper column, known also as the oxygen (low pressure) column. En route to the upper column, the liquid passes through the hydrocarbon adsorber containing silica gel to remove unsaturated hydrocarbons and through a pressure dropping Joule-Thompson valve that gives added refrigeration. At its now lower temperature and pressure, this stream of rich liquid becomes the refrigerant in the crude argon column producing the reflux needed there. Rich liquid then enters the oxygen column somewhere near the middle at a pressure of ~150 kPa (22 psia).

Of all the gases in the oxygen column, nitrogen is the most volatile and streams to the top where it is removed as a product, waste gas, or for recycle purposes. Oxygen flows to the bottom carrying dissolved traces of Kr and Xe, which may concentrate to the sum of 10 ppm. These gases remain dissolved because of their much higher boiling points. Owing to differences in pressure between the two columns, heat flowing from nitrogen in the lower column causes the nitrogen there to condense, while on the upper side of the heat exchanger, the same heat causes the oxygen to boil (hence named the reboiler) to keep the rectification process active. Krypton and xenon may be tolerated as trace inert contaminants in the oxygen. To be recovered they must be substantially concentrated in the separate krypton–xenon column shown. Traces of hydrocarbons and nitrous oxide also concentrate with the heavy rare gases and, because the liquid is almost pure oxygen, it is necessary for safety to operate some continuous method of hydrocarbon removal. Removal is most frequently effected by adsorption, but it can also be achieved by catalytic combustion or by a combination of both. Flows must be adjusted to keep the concentration below the lower flammable limit but high enough to make removal efficient. In a succession of distillation and purification steps, the Kr–Xe crude may be concentrated to as much as a 98–99.9% mixture, the balance being small amounts of oxygen and trace amounts of other atmospheric contaminants.

This krypton–xenon mixture is usually sent to a different location for separation by distillation and further purification by catalytic and/or adsorptive processes in combination with distillation.

4.4. Argon Separation and Purification.

Argon, more volatile than oxygen and less volatile than nitrogen, concentrates in oxygen to perhaps 10% at an intermediate level in the low pressure column. From this point, which is determined by design, operational variables, and analysis, it is withdrawn into the argon concentration column, where the system, now simplified to two components, can be more effectively distilled. Beyond 98%, however, the 3 K difference in boiling points makes other means of oxygen removal practical. As indicated in Fig. 5, the condenser of the argon column is conveniently refrigerated by rich liquid, condensing oxygen that, depleted of argon, returns to the column for further rectification.

Final purification of argon is readily accomplished by several methods. Purification by passage over heated active metals or by selective adsorption (77) is practiced. More commonly argon is purified by the addition of a small excess of hydrogen, catalytic combustion to water, and finally redistillation to remove both the excess hydrogen and any traces of nitrogen (see Fig. 5) (see EMISSION CONTROL, INDUSTRIAL). With careful control, argon purities >99.999%.

The removal of 2% oxygen requires more equipment and is costly in material usage and operating expenses. Industry is attempting to reduce these costs via several approaches. By improving the argon column the oxygen impurities can be reduced to <10 ppmv. This can be coupled with an improvement in the efficiency of the low pressure column to remove most of the nitrogen impurities (78,79). This allows the production of pure argon without the crude argon compressor, a Deoxo-type unit, and the pure argon distillation column.

Another variation would be to improve the argon column to produce argon containing considerably <1% by volume of oxygen that could be removed by catalysis. The need for the catalysis and reaction gases can be removed by using adsorbents to remove the nitrogen and oxygen impurities from the crude argon (80).

Argon also can be recovered from the spent gases remaining from air-consuming processes such as the production of hydrogen by reforming natural gas (see HYDROGEN) or from ammonia synthesis (see AMMONIA) in which argon is concentrated both in the production of the hydrogen and the nitrogen (81).

4.5. Neon–Helium Separation and Purification.

As indicated earlier, neon, helium, and hydrogen do not liquefy in the high pressure (nitrogen) column because these condense at much lower temperatures than nitrogen. As withdrawn, the noncondensable stream has a neon–helium content that varies 1–12% in nitrogen, depending on the rate of withdrawal and elements of condenser design and plant operation.

In the neon column, the nitrogen content is reduced by passing the 620–720 kPa (90–104 psia) stream through a column under reflux with some colder, lower pressure nitrogen obtained from the top of the upper oxygen column. A composition typical of the resulting crude neon is 52% neon, 18% helium, 2% hydrogen, and balance nitrogen, although it varies with adjustments and plants. The crude neon may be vented to the atmosphere or processed in a neon separator and stored as compressed gas to await final purification. With only $18 \times 10^{-6}\,\mathrm{m}^3 (6.4 \times 10^{-4}\,\mathrm{ft}^3)$ neon and $5.5 \times 10^{-6}\,\mathrm{m}^3 (1.9 \times 10^{-4}\,\mathrm{ft}^3)$ of helium in each cubic meter (35 ft^3) of air entering the air separation process, the small quantities of crude collected in even a large air separation unit may be easily appreciated. It is sometimes desirable, therefore, to combine crudes collected from several air plants and to process them at a centralized location in specialized equipment.

Resolution of the noncondensable gas mix may be accomplished in a variety of ways, pure neon being the usual objective. In some processes, hydrogen is removed by catalytic oxidation, sufficient oxygen being introduced for the purpose; by diffusion through palladium; or by fractional adsorption on cold charcoal. Any water formed must be frozen out or removed by adsorptive drying. Most of the nitrogen is commonly removed by liquefaction from the pressurized crude in a liquid-nitrogen-cooled trap, followed by adsorption on liquid-nitrogen-cooled charcoal. Cold, well-activated charcoal completely adsorbs all gases other than neon and helium. Neon itself does adsorb on charcoal to some small extent, whereas helium adsorption is negligible. The final product of these steps, frequently called first-run neon, approximates 75% neon, 25% helium, and is free of all other gases. In older processes, this mixture was finally separated by differential adsorption on cold charcoal. With the increasing availability of neon crudes and very low temperature refrigeration processes, equipment in which the neon is condensed, near its boiling point has come into increased use. The liquid neon first appears at purities that exceed 99.995% the sole residual impurity being helium. The residual helium can be allowed to evaporate from the liquid neon further, purifying neon to 99.999% purity.

The uncondensed helium contains substantial amounts (up to 10%) of pure neon as its only diluent. Neon can be removed completely by additional fractional condensation followed by adsorption of neon on charcoal at temperatures $<77\,\mathrm{K}$. In the United States, economics favor wasting most of this atmospheric helium. It remains of interest, however, because it contains $\sim$10 times as much helium-3 as does helium from natural gas. Additionally, if helium-bearing natural gases become depleted, the atmosphere is expected to be the only remaining source. There has been much speculation about dedicated plants required to produce helium when natural-gas sources are exhausted, and some designs have been made. Only one plant is known to have been built exclusively for helium. That plant, put into operation in Germany in 1972 (82), obtains helium from ammonia synthesis gases.

4.6. Krypton–Xenon Purification and Separation. Highly concentrated Kr–Xe crudes are purified by removing residual hydrocarbons, CO_2 and

H_2O, and other atmospheric components; and then are separated to produce krypton and xenon. Inert atmospheric pollutants may survive the many steps of the purification process (83). In particular, tetrafluoromethane [75-73-0], CF_4, is sometimes found in pure krypton to the extent of a few parts per million (see FLUORINE COMPOUNDS, ORGANIC) indicating an atmospheric level of CF_4 on the order of 10^{-2} ppm. It has been postulated that CF_4 results from the reaction of carbon with flurospar, CaF_2, in the reducing gases of iron (qv) smelters. Removal of CF_4 from Kr can be accomplished by proprietary processes when its presence is detrimental to the intended use of the Kr. Crude Kr–Xe mixtures have also been found to contain varying levels of other halogenated compounds, oxides of nitrogen, and random impurities.

Krypton and xenon are recoverable from large air-separation units (>1000 tons/day) due to the small quantities present in air and expensive additional processing equipment. Limited quantities are produced with much more effort. In European countries and the CIS, certain plants have been designed for the selective recovery of krypton and xenon from air. Several types of processes have been designed and constructed (84), but basic to all of them is the scrubbing of very large quantities of air using a relatively small quantity of liquid air. The krypton–xenon content of a large volume of air is thus concentrated and can be more readily and economically refined. Similarly, as for the argon and helium sources discussed above, air-consuming processes concentrate Kr–Xe and thus become attractive sources. Although many patents have been issued, only a few plants have been built. Purification details depend on the quality of the crude.

4.7. Krypton and Xenon from Nuclear Power Plants. Both xenon and krypton are products of the fission of uranium and plutonium. These gases are present in the spent fuel rods from nuclear power plants in the ratio 1 Kr/4 Xe. Recovered krypton contains ~6% of the radioactive isotope Kr-85, with a 10.7 year half-life, but all radioactive xenon isotopes have short half-lives.

Separation of krypton and xenon from spent fuel rods should afford a source of xenon, technical usage of which is continuously growing (85). As of this writing, however, reprocessing of spent fuel rods is a political problem (see NUCLEAR REACTOR TYPES). Xenon from fission has a larger fraction of the heavier isotopes than xenon from the atmosphere and this may affect its usefulness in some applications.

4.8. Radon Separation. Owing to its short half-life, radon is normally prepared close to the point of use in laboratory-scale apparatus. Radium salts are dissolved in water and the evolved gases periodically collected. The gas that contains radon, hydrogen, and oxygen is cooled to condense the radon, and the gaseous hydrogen and oxygen are pumped away.

5. Commercial Distribution

Commercially pure (>=99.997%) helium is shipped directly from helium-purification plants located near the natural gas supply to bulk users and secondary distribution points throughout the world. Commercially pure argon is produced at many large air-separation plants and is transported to bulk users up to several hundred kilometers away by truck, by railcar, and occasionally by dedicated gas pipeline (see PIPELINES). Normally, only crude grades of neon, krypton, and xenon are produced at air-separation plants. These are shipped to a central purification facility from which the pure materials, as well as smaller quantities and special grades of helium and argon, are then distributed. Radon is not distributed commercially.

The noble gases are distributed as gaseous and cryogenic liquid products in containers having capacities ranging from $>0.001\,m^3$ ($0.035\,ft^3$) to $\sim 45{,}000\,m^3$ ($1.6 \times 10^6\,ft^3$).

Most gaseous products are distributed in forged steel or aluminum alloy cylinders at high pressure, typically 15 MPa (2200 psi), but ranging from 6 to 41 MPa (900–6000 psi). Small quantities of research-grade materials are still sold in glass flasks at atmospheric pressure. The (U.S.) Compressed Gas Association (CGA) specifies different cylinder valve connectors for different types of gases. For the noble gases the connectors used are CGA 100 for lecture bottles, CGA 580 for 21 MPa (3000 psig), CGA 680 for 24 MPa (3500 psig), and CGA 677 for 41 MPa (6000 psig) cylinders.

For distributing larger quantities of gaseous helium, argon, and occasionally neon, a number of large, horizontal, compressed gas cylinders are manifolded on truck semitrailers (called tube trailers) or railroad cars. Like individual cylinders, these serve both as transport containers and rental storage containers. Capacities of tube trailers range from ~ 300 to $5200\,m^3$ ($10{,}000$–$185{,}000\,ft^3$) of gas.

Bulk quantities of helium and argon and smaller quantities of neon are distributed as cryogenic liquids in insulated containers of liquid capacities of 10–56,000 L (2.5–14,800 gal). Although the cryogenic refrigeration of the liquid is sometimes utilized as for magnetic resonance imaging (MRI), another justification for this mode of distribution is the lower transportation costs resulting from reduced ratios of shipping container weight to product weight (see IMAGING TECHNOLOGY). This factor is particularly important for such a low density material as helium. For example (86), the weight of compressed-gas cylinders is ~45 times that of their helium content; on the other hand, the weight of a 500-L cryogenic liquid container is only about eight times the weight of the helium, and large liquid-helium semitrailers are only about four times heavier than their helium load.

Because of liquid helium's uniquely low temperature and small heat of vaporization, containers for its storage and transportation must be exceedingly well insulated. Some containers are insulated with only a fairly thick layer of very efficient insulation, but containers with the least heat leak use an inexpensive sacrificial cryogenic liquid, usually liquid nitrogen, to shield thermally the liquid helium contents.

Two types of insulation are used in liquid helium containers. Simple high vacuum insulation, exemplified by the common Thermos bottle, consists of a well-evacuated space between highly reflective walls; however, its limited effectiveness restricts its use to liquid nitrogen-shielded containers. Highly effective, evacuated multilayer insulations are constructed from laminar arrangements of many radiation shields, metal foil or metal-coated plastic film, in a vacuum envelope. Thermal contact between shields is minimized either by interposing a low conductivity, fibrous separating membrane between shields or, in the case of coated plastic film, by crinkling the film so that adjacent layers touch only at a few, discrete, comparatively widely spaced points. A third type of cryogenic insulation, evacuated, low density, mineral powders, such as expanded perlite, is not often used in liquid helium containers but it is used for large, liquid argon vessels.

Most small liquid helium containers are unpressurized: heat leak slowly boils away the liquid, and the vapor is vented to the atmosphere. To prevent plugging of the vent lines with solidified air, check valves of some sort are included in the vent system. Containers used for air transportation are equipped with automatic venting valves that maintain a constant absolute pressure with the helium container in order to prevent liquid flash losses at the lower pressures of flight altitudes and to prevent the inhalation of air as the pressure increases during the aircraft's descent. Improved super insulation has removed the need for liquid nitrogen shielding from almost all small containers.

For shipping large (>5000 L) quantities of liquid helium over great distances, nonvented pressurized containers are used. At the purification plant continers are filled with liquid helium at the atmospheric boiling point. As heat leaks into the container, no product is vented; instead the pressure is allowed to build up as the fluid temperature increases. It may occur the interior pressure and temperature are above the critical point upon arrival at the destination, and the contents are no longer a liquid but a cold, dense, supercritical fluid. However, by careful venting procedures, a substantial part of the contents can be recovered as liquid, and the vented vapor is compressed into cylinders. For deliveries involving only a week or so transit time, eg, deliveries with the continental United States, large trailers with heat leaks limited to ~30 W by evacuated multilayer insulation are used. For more extended shipments, eg, by ocean freighter from the United States to Japan, which may involve nearly a month's transit time, up to 40,000-L capacity, truck-transportable containers are used. Their heat leak is held to ~8 W by a combination of liquid-nitrogen shielding and evacuated multilayer insulation, and their liquid-nitrogen consumption is ~40 L/day.

Liquid argon is distributed by truck from the point of production using large cryogenic tank trailers similar to those used for liquid oxygen and nitrogen. At each stop on the delivery route, liquid argon is transferred into fixed, well-insulated, cryogenic storage tanks called customer stations from which gaseous or liquid argon is withdrawn as needed (see CRYOGENIC TECHNOLOGY; INSULATION, THERMAL).

6. Economic Aspects

U.S. production statistics for high purity helium are listed in Table 4. The peak in production during the 1960s reflects the large helium usage by the U.S. space program. Most of this production was by the U.S. Bureau of Mines. Private plants began significant production in 1963.With the enactment of the Helium Privatization Act of 1996, U.S. government production of high purity helium was discontinued in 1998.

During the 1980s, the market for U.S. produced helium grew at an average annual rate of 9%. During the 1990s, U.S. helium production increased at an

Table 4. **Annual U.S. Production and Exports of High Purity Helium, 10^6 m^{3}[a,b,c]**

Years	Production Bureau of Mines	Private Plants	Total	Exports
1960–1964	16.7	0.5	17.2	0.1
1965–1969	16.7	7.3	24.0	1.6
1970–1974	5.2	12.9	18.1	3.4
1975–1979	5.7	20.1	25.8	5.2
1980–1984	7.2	30.6	37.8	10.3
1985–1989	9.3	55.0	64.3	15.8
1990–1994	8.8	83.9	92.7	27.1
1995	7.2	88.9	96.1	27.7
1996	6.1	88.6	94.7	22.8
1997	5.3	102.0	107.3	29.5
1998	2.0	110.0	112.0	27.8
1999	0.0	117.0	117.0	26.8
2000	0.0	126.6	126.6	37.0
2001	0.0	131.9	131.9	43.0
2002	0.0	127.1	127.1	39.5
2003	0.0	122.0	122.0	41.3

[a] To convert 10^6 m^3 to 10^6 ft^3, multiply by 35.3.
[b] Ref. 87.
[c] Values for time periods exceeding 1 year are average values.

average annual rate of ~3.2%/year. From 2000 through 2003, the growth rate for U.S. produced helium has been negative, largely due to a general economic downturn coupled with a decline in the production of optical fiber and the grounding of the U.S. space shuttle, two fairly significant helium applications.

Exports of helium started in the early 1960s, and became a significant fraction of total production only after the development of equipment and techniques for transoceanic shipment of bulk liquid helium. The foreign market made up ~31% of U.S. helium sales in 1991 and ~34% in 2003. However, exports of U.S. helium are expected to slow in the future and decrease significantly as sources of helium are developed in geographies closer to foreign markets. For example, two new helium plants are scheduled to commence operations in 2005, one in Qatar and one in Algeria. Both of these facilities will recover helium from the waste stream of LNG production and once operational, will supply helium to Asian and European markets, further reducing U.S. exports to those geographies.

At some yet to be determined point in the future, it is quite likely that the United States will become a net importer of helium. There are a number of factors that will determine when this will happen, not the least of which is the decline rate of the Hugoton natural gas field, a primary source of current U.S. helium production. Other factors, such as the development of new sources of helium (both in the U.S. and in other parts of the world), the growth rate of current helium applications, and the development of new applications and technologies will all have an impact on the status of U.S. helium production.

The U.S. production of argon is summarized in Table 5. Because argon is a by-product of air separation, its production is ~1% that of air feed.

Table 5. **Annual U.S. Production of Argon**[a]

Years[b]	Production, 10^6 m^3[c]
1960–1964	23.1
1965–1969	54.5
1970–1974	105.3
1975–1979	173.4
1980–1984	237.5
1985–1989	318.4
1990–1994	401.7
1995–1999	512.4
2000	589.4
2001	522.0
2002	528.6
2003	607.9

[a] Ref. 88.
[b] Values for time periods exceeding 1 year are average values.
[c] To convert 10^6 m^3 to 10^6 ft^3 multiply by 35.3.

Comparative prices of noble gases in 2004 are listed in Table 6. The prices for Ne, Kr, and Xe dropped significantly from 1990 as a result of Russian exports of noble gases. Prices in 1990 were \$120/m^3 for Ne, \$700–800/m^3 for Kr, and \$5750–8750/m^3 for xenon.

7. Specifications and Standards

In the United States, government agencies and trade organizations have established standards and specifications for helium and argon (Tables 7 and 8).

Table 6. **2004 U.S. Prices of Noble Gases**

Gas	Price[a], \$/m^3
Bulk quantities	
helium	
gas	
USBLM Crude Helium (October 2004)	1.96
private	1.77–2.88
liquid	
private	2.30–2.70
argon	0.76
Laboratory quantities	
helium[b]	4.20–4.90[c]
	22.30–44.90[d]
argon[b]	2.70–8.50
neon	60–120
krypton	400–500
xenon	4000–5000

[a] To convert \$/m^3 to \$/ft^3multiply by 0.0283.
[b] Varying purity levels.
[c] Industrial grade.
[d] Laboratory quality.

Table 7. **Selected Commercial Specifications for Helium Compressed Gas Association Grades**[a]

Specification	L	N	P	G
minimum purity, %	99.995	99.997	99.999	99.999
maximum impurities, μL/L				
total	50	30	10	1
water	15	3	1.5	
THC as CH_4[b]		1	0.5	
oxygen	5	3	1	
nitrogen + argon		5[c]	5	
neon		23	2	
hydrogen		1	1	
CO/CO_2			0.5	

[a] Ref. 89.

[b] Total hydrocarbons (THC) reported as methane.

[c] Maximum 5 μL/L nitrogen only.

Typical commercial purities for neon, krypton, and xenon are shown in Table 9. In general, all grades delivered from a given facility are prepared from a single product stream. The differences between grades lie in the care taken in subsequent handling, ie, the preparation of containers, elimination of intrusion of air and other gases, and the sampling and analytical efforts. These factors ensure the quality of the gas but add to its cost. Because all other substances are solid at liquid helium temperatures, liquid helium filtered through a nominal 10-μm filter is accepted as pure helium.

8. Analytical Methods

The most common techniques for measuring the concentrations of noble gases in mixtures are gas–solid chromatography (qv) (91) and mass spectrometry (qv) (92). The sensitivity of both techniques can be increased many-fold by

Table 8. **Selected Commercial Specifications for Argon Helium Compressed Gas Association Grades**[a]

Specification	C	D	E	F
minimum purity, %	99.997	99.998	99.999	99.9985
maximum impurities, μL/L				
total	30	20	10	15
water	10.5	3.5	1.5	1
THC as CH_4[b]	1	0.5	0.5	0.5
oxygen	5	2	1	2
nitrogen	20	10	5	10
hydrogen				1
carbon dioxide	1	0.5	0.5	0.5[c]
carbon monoxide				

[a] Ref. 90.

[b] Total hydrocarbons (THC) reported as methane.

[c] Combined carbon dioxide and carbon monoxide.

Table 9. **Purities of Commercial Neon, Krypton, and Xenon**[a]

Purity	Neon	Krypton	Xenon
minimum purity, %	99.999	99.999	99.999
maximum impurity, μL/L			24.0
total	10	10	10
helium	8		
xenon		2	
krypton			3
nitrogen	2	3	3
oxygen	0.5	1	0.5
CO/CO_2	0.5	2	1
THC as CH_4[a]	0.5	1	0.5
water	1	1	0.5

[a] Total hydrocarbons (THC) reported as methane.

concentrating the noble components by such methods as selective adsorption (qv) or removal of the noninert components using hot reactive metals (90) or other gettering means.

The determination of impurities in the noble gases is also accomplished by physical analytical methods and by conventional techniques for measuring the impurity in question (93), eg, galvanic sensors for oxygen, nondispersive infrared analysis for carbon dioxide, and electrolytic hygrometers for water.

9. Uses

In 2003, the primary domestic uses of helium were magnetic resonance imaging and other cryogenics (28%), pressurizing and purging (26%), welding (qv) (20%), and controlled atmospheres (13%). Other uses included leak detection (4%), breathing mixtures (2%), and others, such as lifting gas, heat transfer, optical fiber manufacture, etc (94).

The main uses for argon are in metallurgical applications and in electric lamps. Neon, krypton, and xenon, because of high costs, are limited to specialized uses in research, lasers instrumentation, electric lighting, satellite propulsion, window thermal insulations, refrigeration and other high tech applications. There are no significant technical uses for radon.

9.1. Metallurgical. To prevent reaction with atmospheric oxygen and nitrogen, some metals must be shielded using an inert gas when heated or melted (95). Applications in metals processing account for most argon consumption and an important part of helium usage.

In gas tungsten-arc welding (96), also called tungsten inert gas (TIG) welding, the nonconsumable tungsten electrode, hot filler metal, and weld zone are protected by a continuous stream of helium, argon, or their mixtures. The arc is struck between the electrode and the workpiece. Helium shielding produces a hotter arc than does argon shielding. When the electrode is positive and argon or a predominantly argon mixture is used for shielding, a cleaning action occurs on the surface of the weld zone that does not occur with a shield of helium. Argon-shielded, alternating current (ac) arcs produce the same surface-cleaning action, and the electrode has a higher current-carrying capacity than a continuously positive electrode. Helium shielding, however, decreases the stability of ac arcs.

In gas metal-arc, also called metal inert gas (MIG) welding, the arc is struck between the workpiece and a metal electrode that is consumed as it is transferred in the form of molten droplets across the arc into the weld joint. Using a predominantly argon shield gas, the droplets are transferred with little radial dispersion. Using pure helium, on the other hand, the droplets are larger and have more of a tendency to spray radially from the arc's axis.

Helium is finding use as a fluidizing transport medium for an emerging application known as col spray or cold gas dynamic spraying, that is a method of applying a coating of particles to a substrate. This technology was discovered in Russia in the early 1990s and subsequently patented in the United States in 1994 as U.S. Patent No. 5,302,414 (9). Small particles of 1–50 μm are accelerated in a gas stream to a velocity of 300–1200 m/s and directed as a substrate. Low temperatures below 400°C are used. The upon impact with the substrate the particles plastically deform, resulting in a dense coating with the properties of the coating similar to the properties of the original particals. This contrasts with other thermal spray technologies in which high heat input into the process results in thermal changes to the coating. Although different gases can be used for this technology, helium is desirable because of its high sonic velocity that allows the particles being sprayed to achieve higher kinetic energies.

Argon, helium, and their mixtures with other gases are used as the working fluids in plasma arc devices for producing plasma jets with temperatures in excess of 50,000 K. These devices are used for cutting metals and for spray coating of refractory alloys and ceramics (qv) (see PLASMA TECHNOLOGY).

Large quantities of argon are used in the argon–oxygen decarburizing (AOD) process for stainless-steel production (97). A charge containing stainless and carbon-steel scrap and low cost, high carbon ferrochrome is melted in an arc furnace and then bottom-blown with an argon–oxygen mixture in a separate AOD vessel. The oxygen performs the necessary decarburizing, and the argon serves to reduce the partial pressure of the carbon monoxide reaction product, thereby selectively increasing the rate of carbon oxidation relative to that of chromium. Because of the arc furnace's lower materials costs, reduced chromium losses, and increased productivity, >90% of United States stainless-steel production is by the AOD process (87) (see STEEL).

Argon bubbles are frequently used to stir iron and steel ladles to prevent stratification, to help remove dissolved gases, to remove potential inclusion by flotation (qv), and to control temperatures. Argon is used as an inert blanket in melting, casting, and annealing certain alloys. Helium and argon environments are used for high temperature refining and fabrication of specialty materials such as zirconium, niobium, tantalum, titanium, uranium, thorium, plutonium, and reactor-grade graphite. Some furnace brazing, soldering, and powder-metal sintering operations (98) use helium and argon atmospheres either alone or in mixtures with hydrogen when a reducing atmosphere is required. Jets of argon can be used to atomize molten reactive metals to produce metal powders (99). In some metallurgical reactions, argon or helium is used as a carrier to transport products to and from the reaction zone and as an inert diluent to modify reaction rates. Typical applications are the Kroll process for making zirconium and titanium (100) and the submerged injection of pulverized reagents such as lime and calcium carbide into molten steel.

For furnace applications the noble gases find novel uses. Argon is used to blanket motlen pure titanium, as other less expensive gases like nitrogen, can react with the metal. In this application, the argon and also be used to relieve the vacuum in vacuum furnaces. Similarly helium is finding use as a quench gas in vacuum furnaces. Helium's high heat transfer characteristics increases quench speed and can shorten furnace production cycles and improve the properties of the melt material.

Low pressure argon is the usual medium for industrial sputtering of metals and other solid films (101) (see THIN FILMS, FILM FORMATION TECHNIQUES).

9.2. Laboratory and Scientific. The noble gases are closely associated with precision measurement techniques. The international standard of length, the meter, is defined in terms of a spectral line of krypton-86. The boiling point of neon is a defining point on the international practical temperature scale (102). The vapor pressures of the two helium isotopes, helium-3 (18) and helium-4 (103), furnish an internationally recognized temperature scale $<5.2\,\mathrm{K}$, and the vapor pressures of neon (17), argon (104), krypton (24), and xenon (25) afford convenient and reliable secondary temperature scales. Precision gas thermometers, one of the fundamental devices for defining temperatures, normally use helium as a fill gas because of its small deviations from ideal gas behavior (see TEMPERATURE MEASUREMENT). Quantum superconducting devices (SQUIDs) are used increasingly for precise and fundamental measurements, and the small, neon–helium, continuous-wave lasers (qv) are widely used for interferometric techniques and for precision alignments ranging from laboratory equipment to large tunnel bores.

Helium is the most commonly used carrier gas for gas–liquid and gas–solid chromatography (105). It is chemically inert and minimally dissolved or adsorbed on the column packing. Its low viscosity and density minimize pressure drop. But its primary advantage is that, because of its low molecular weight, its physical properties differ greatly from those of most materials being analyzed. Using a helium carrier thus yields maximum sensitivity for detectors based on changes in thermal conductivity, sonic velocity, density, etc. Argon is also used as a carrier gas, especially when analyzing samples containing hydrogen or in regions outside the United States where helium is more expensive. Thermal conductivity detectors, particularly, respond in a highly nonlinear fashion to hydrogen peaks in a helium carrier.

The helium leak detector is a common laboratory device for locating minute leaks in vacuum systems and other gas-tight devices. It is attached to the vacuum system under test; a helium stream is played on the suspected leak; and any leakage gas is passed into a mass spectrometer focused for the helium-4 peak. The lack of nearby mass peaks simplifies the spectrometer design; the low atmospheric background of helium yields high sensitivity; helium's inertness ensures safety; and its high diffusivity and low adsorption make for fast response.

Detectors for ionizing radiation use the noble gases; mixtures containing neon, argon, and helium are used in Geiger-Muller counters; argon and xenon are used in proportional counters; and electron avalanche in liquid xenon (106) is the basis for very accurate photon detection (see PHOTODETECTORS). In neutron detectors, helium-3 has a high cross section to neutrons for the formation of tritium whose decay is then detected by a conventional counter (4). Krypton is frequently used to determine surface areas of fine solids by adsorption techniques. And helium and argon are often used as protective atmospheres when working with highly reactive materials.

9.3. Light Sources. In common incandescent lamps, the metal filament, usually tungsten, is protected by a glass bulb filled with a gas mixture, usually argon–nitrogen (107,108). Argon's higher molecular weight compared to nitrogen's helps reduce the rate of sublimation of the glowing tungsten filament, thereby prolonging its life, and argon's lower thermal conductivity reduces thermal losses, thereby improving the electrical efficiency. The arcing tendency of argon, however, necessitates the use of some (typically 12%) nitrogen in the fill gas. Krypton's still higher molecular weight and lower thermal conductivity makes it technically superior as a fill gas, but its higher cost has limited use to long-life lamps and to those parts of the world where electrical energy is especially expensive. Krypton-filled light bulbs are common on the U.S. consumer market and in automotive lighting. Halogen lights for home use are finding increasing application.

In automotive lighting, rare gases are commonly used. Traditionally krypton has been used either as a pure gas or in combination with other gases, like nitrogen, argon, or methyl bromide, to fill the cavity of automotive light bulbs. In recent years xenon has found increasing use in automotice headlights. The xenon produces a bright blue-white light that many drivers find desirable. Inititially xenon headlights were only found on high end luxury automobiles, but they are becoming increasingly commonplace.

Low pressure gas-discharge tubes consist of a sealed glass tube with an electrode at each end and a filling of gas at ~1 kPa (0.15 psia) absolute pressure. When a sufficiently high, alternating voltage is impressed across the tube, a low pressure plasma fills the tube bore and emits radiation at wavelengths dependent primarily on the composition of the fill gas. A familiar form of this light source is the neon sign used for advertising displays, a term that has been generalized to include any colored tubular lighting display regardless of the fill gas used. In clear glass, pure neon yields a red-orange light; helium produces a yellowish-white; argon emits a bluish color; helium–argon forms an orange tint; and neon–argon makes a deep lavender glow. By using these various filling gas mixtures in conjunction with colored glass tubes and sometimes a bit of mercury vapor, practically the entire spectrum of colors can be produced (107). Small, low pressure gas-discharge bulbs are widely used for indicator lights.

In fluorescent light bulbs xenon is being considered as a replacement for the mercury found in these bulbs. The mercury is considered environmentally hazardous and alternatives to reduce its usage. The ionization properties of xenon would facilitate giving rise to the generation of light in the fluorescent bulb.

Neon, argon, and krypton are used to initiate and sustain the arc in metal-vapor discharge tubes, notably various mercury- and sodium-vapor lamps. The most familiar of these are the tubular fluorescent lamps in which a mercury-vapor discharge produces radiation that is converted to visible light by a phosphor coating on the tube wall. Most fluorescent tubes are filled to roughly 500 Pa (0.07 psia) absolute pressure with about a half-and-half mixture of argon and krypton. Krypton produces the greatest luminous efficiency, but it can be troublesome to start. Neon yields the greatest absolute light output, but it requires a higher starting voltage and tends to erode the electrodes by ion bombardment. Argon is used to start the arc and vaporize the mercury in high pressure mercury-arc lamps, and neon performs the analogous function in high pressure sodium-vapor lamps. Xenon, with or without mercury, is used at relatively high pressure in short-arc lamps that provide a highly concentrated light source.

Intense and brief light pulses are obtained by discharging a capacitor through xenon-filled flash lamps. Small lamps of this type are widely used for photography because light color approximates daylight, and the brief light pulse (about a millisecond duration) effectively freezes all motion. Stroboscope lamps are similar to flash lamps, but are designed for repetitive discharges. Although xenon produces the greatest light intensity, neon is frequently used because of the contrast to daylight provided by its red color.

The noble gases are used throughout laser technology (109). From the first, large xenon flash lamps have been a common means for exciting pulsed lasers, such as the ruby and neodymium glass devices. The neon–helium continuous lasers are widely used for optical applications that require neither high efficiency nor powers above a fraction of a watt. The simplicity and reliability derived from the use of a low pressure, glow discharge for excitation plus the perfect chemical stability of the lasing medium account for the popularity of these devices. Noble-gas ion lasers operate at very high power densities and over a wide frequency range (110). Carbon dioxide lasers are the most powerful and efficient of the common continuous lasers; the lasing gas is a carbon dioxide mixture which, among several other components, includes helium to increase gas cooling rates (111). Excimer lasers use a rare gas combined with a halogen donor to form “dimers” that spontaneously emit radiation. Eximer lasers generated dimers such as ArF, KrF, and XeCl, with different wavelenghts produced. Specific wavelengths are then matched to the application at hand. Eximer lasers have been used in a variety of applications, including corneal sculpting, and are finding increasing use in electronic chip manufacture, where the laser is used in the chip etching process.

The efficiency of a helium–neon laser is improved by substituting helium-3 for helium-4, and its maximum gain curve can be shifted by varying the neon isotopic concentrations (4). More than 80 wavelengths have been reported for pulsed lasers and 24 for continuous-wave lasers using argon, krypton, and xenon lasing media (112) (see LASERS).

9.4. Electronic. The largest use of noble gases in the electronics industry is for the manufacture of semiconducting devices. The starting materials, single crystals of ultrapure semiconductors (qv), such as silicon or germanium, are grown from melts using helium or argon as both a protective atmosphere and a heat-transfer medium. Only these very pure and inert gases can ensure the extremely high crystals purities required. These same inert gases are also used as diluents and carriers for the dopant gases such as arsine or phosphine used to form the *n* and *p* regions in the semiconducting devices.

Semiconducting devices have replaced many of the gas-filled electronic tubes, and this use for the noble gases continues to dwindle. Helium, neon, and argon are still used in certain high voltage switching and regulating tubes and for some lightning arrestors. Traces of krypton-85 are used in some of these tubes to furnish a continuous supply of gas ions which serve to stabilize the starting voltage. Recently, xenon has found use as a plasma in the deep trench etching of DRAM chips. New small chip geometries necessitate more precise etching, something the xenon plasma enables by permitting a more focused etch process.

9.5. Cryogenics. The usefulness of a substance as a low temperature working fluid is limited by its boiling point and freezing point. Cost and safety must also be considered. Krypton, xenon, and radon are seldom used as cryogenic fluids. Boiling argon is occasionally used for isothermal baths near the oxygen boiling point where oxygen might be too hazardous. Similarly, liquid-neon baths are sometimes used when the use of liquid hydrogen is judged to be too dangerous. However, both gaseous and liquid helium are quite widely used in cryogenic applications (see CRYOGENIC TECHNOLOGY).

The most common application of liquid helium is in superconducting magnets, where some 25% of the worlds helium is used. In particular, magnet resonance imaging, or MRI, has become commonplace as a medical diagnostic tool after its commercialization in the mid 1980s. Some 14,000 high field MRI units that use liquid helium are installed worldwide. The liquid helium acts as a refrigerant for the superconductive magnet that becomes superconductive at liquid helium temperatures. The superconductive magnet develops a strong magnetic field, measured in Teslas, that aligns the hydrogen atoms in the patients body. The deflection to the magnetic field can be interpreted by sophisticated electronics to develop an anatomical image. The typical wire used in these systems is neodymium doped titanium in a copper carrier. Research has developed "high temperature" superconducting materials that are superconductive at liquid nitrogen temperatures, however, these materials have proven to be too brittle to form into wire.

Gaseous helium is commonly used as the working fluid in closed-cycle cryogenic refrigerators because of chemical inertness, nearly ideal behavior at all but the lowest temperatures, high heat capacity per unit mass, low viscosity, and high thermal conductivity.

Below hydrogen's triple point temperature of 13.80 K, only helium exists as a dense fluid, and at lower temperatures, it is the only substance that retains appreciable heat capacity. Many cryogenic systems operate near the 4.22 K boiling point of helium-4. Lower temperatures can be maintained using vacuum pumps to lower the boiling pressure; however, once the superfluid transition occurs, the Rollin film phenomenon severely impedes the pumping process making it very difficult to attain temperatures much <1 K by this technique (113). Helium-3 is more volatile than is helium-4, and in the range of interest, its use is not complicated by the Rollin film. By boiling liquid helium-3 under vacuum, temperatures down to ~ 0.25 K can be attained (114). Helium-3 dilution refrigerators can be operated in either batch or continuous mode (59) and can reach temperatures as low as 0.005 K (115). Adiabatic helium-3 compression refrigerators based on the Pomeranchuk effect can produce temperatures <0.002 K (38), the lowest temperatures presently attainable by mechanical means. Still lower temperatures are produced by various adiabatic demagnetization processes precooled with one of the helium refrigeration processes.

Several applications of cryogenic temperatures are based on properties that vary more or less smoothly with temperature. The electrical conductivity of pure metals increases as the temperature is lowered, allowing cryogenically cooled, normal metals (aluminum, copper, or sodium) to be used for electromagnets (116) and in electrical power distribution (117). The vapor pressures of all substances decrease with decreasing temperature; at the helium boiling point, only helium itself retains any substantial vapor pressure. Helium-cooled panels form cryopumps used for high capacity vacuum pumping systems or for smaller systems where very clean pumping is required (118). Even residual helium gas can be removed effectively by an adsorbent, such as activated charcoal cooled to helium temperature. Large cryopumps are used to sustain vacuums in the space-simulation chambers and in the neutral-hydrogen beam injectors and plasma chambers of experimental hydrogen fusion reactors (119,120). The thermal noise in electrical components decreases at low temperature. Many radio, and other radiation-detecting devices use neon or helium cooling to enhance their sensitivities (121).

Other applications of cryogenic temperatures involve a phenomenon that does not exist at normal temperatures. A number of metals and alloys abruptly change from normal electrical conductors into superconductors as they are cooled into the helium temperature range. In the superconducting state, all resistance to direct current disappears, and the resistance to alternating currents becomes very small. The current density and magnetic field that a superconductor can sustain increases as the material is further cooled below its transition temperature. Thus the lowest temperatures practical are desirable in most applications of superconductivity.

Large, helium-cooled superconducting electromagnets are used for bubble chambers, for bending and deflecting magnets in particle accelerators, for plasma confinement in fusion reactors, and for magnetohydrodynamic power generators (122). Experimental systems using superconducting coils to levitate high speed vehicles magnetically have been investigated (123). Superconducting windings have been built for motors and generators (124), and experimental superconducting cables have been built for direct (dc) and ac power transmission (122). Smaller superconducting magnets are used for magnetic separating devices (125) and in certain instruments requiring intense, stable, and uniform fields (see SEPARATION, MAGNETIC SEPARATION).

Because of the tonnage quantities of fluid involved (126), large superconducting machinery must be cooled with commercial helium. Most commonly, such machines are cooled by liquid helium boiling near atmospheric pressure. The principal limitations are necessary to provide channels for vapor transport and the film boiling instability if local heat fluxes exceed a critical value (47). Other cooling systems utilize forced-flow convention with single-phase, compressed fluid helium, often called supercritical helium, which does not suffer from a critical heat-flux limitation, but that does have a definite total heat load limitation. A few large systems have been designed for cooling by free convection of compressed fluid helium, by gas–liquid forced convection, and by conduction through superfluid helium (127). Heat- and mass-transfer rates in bulk fluid helium have been concisely reviewed (47).

9.6. Nuclear Reactors. The first-generation of gas-cooled fission reactors used coolant temperatures of only ~400°C that permitted the use of inexpensive carbon dioxide as the coolant gas. For improved thermal efficiency, second-generation reactors were designed to use gas-coolant temperatures up to 790°C, temperatures at which only helium offers the necessary chemical stability, inertness, high heat-transfer rates, low aerodynamic pressure losses, and low neutron cross-section (^{4}He only) (128). Although gas-cooled reactors claim certain operating advantages and relative immunity from loss-of-coolant accidents, only one commercial power generating reactor of this type (Fort St. Vraine, Colorado) is in operation (129).

Different combinations of stable xenon isotopes have been sealed into each of the fuel elements in fission reactors as tags so that should one of the elements later develop a leak, it could be identified by analyzing the xenon isotope pattern in the reactor's cover gas (4). Historically, the sensitive helium mass spectrometer devices for leak detection were developed as a crucial part of building the gas-diffusion plant for uranium isotope separation at Oak Ridge, Tennessee (130), and helium leak detection equipment is still an essential tool in nuclear technology (see DIFFUSION SEPARATION METHODS).

Programs for the development of fusion power provide applications for the noble gases. The magnetic plasma confinement approaches require massive quantities of liquid helium to cool the large superconducting magnets and cryopumps (131). In the laser-ignited, inertial confinement approaches, xenon discharge lamps are a common means for energizing the large pulsed lasers. To improve energy yields, liquid helium is used to freeze the tritium fuel into a uniform, thin solid film on the inner surface of the glass microballoon targets (132) (see FUSION ENERGY).

In particle-track detectors, neon and helium are the common filling gases for spark chambers and streamer chambers (133), and liquid helium, neon, neon–hydrogen mixtures, and xenon have been used in bubble chambers (134). Xenon provides a very heavy target nucleus useful for detecting photons and neutral particles. Because of their similar physical properties, neon–hydrogen mixtures can be used in dual-fluid bubble chambers with liquid hydrogen (135). The liquid neon charge in the 4.6-m diameter bubble chamber at Fermilab (136) probably represents the greatest quantity of neon ever used for a single application.

Helium-3 ions are used as bombarding particles in activation analysis. These ions require less energy than protons, and their limited penetration permits surface analysis only (4). The concentrations of argon-40 accumulated from the radioactive decay of potassium-40 is used to determine the age of minerals and meteorites (4). Hermetically sealed electronic components have been tested for leaks by several hours exposure to a pressurized atmosphere containing a trace of krypton-85 followed by a rapid purge and inspection for residual radioactivity that possibly has leaked into the small containers (137). Krypton-85, because of its freedom from chemical holdup, is sometimes used as a tracer for movements of hydrological sediment flows (137) and for tracking the movement of large air masses (138).

Radioactive isotopes of the helium-group elements also pose some problems in nuclear fission technology. The off-gases from reactors and, more important, from nuclear fuel reprocessing plants, contain many hazardous radioactive materials. The chemically active ones can be removed and concentrated for storage by various chemical means, but these methods are ineffective for the radioisotopes of the helium-group elements. Xenon and krypton are principal products of uranium fission. All of xenon's unstable isotopes and most of krypton's have such short half-lives that they practically disappear after a reasonable detention period. Krypton-85, however, has a half-life of 10.76 year, long enough to make detaining the whole gas stream impractical and short enough to account for its intense radioactivity. Various physicochemical processes for concentrating the krypton fraction for long-term storage have been described (139), but the only processes now operating in the United States rely on cryogenic condensation and adsorption techniques (140).

9.7. Aerospace. Between World Wars I and II, the primary use of helium was as the only safe, nonflammable light gas for lighter than air craft, but in the 1990s this use is very limited. Balloons and blimps are used only for sports and advertising purposes. Many unoccupied weather balloons and upper atmosphere research balloons still use helium, but these could use hydrogen with little hazard were it necessary. For safety, most toy carnival balloons are inflated with helium instead of hydrogen. From time to time, efforts are made to revive commercial lighter-than-air technology for such things as logging and cargo handling, but no such project has yet proved commercially successful.

In rocket and space vehicle systems, helium is used for purging cryogenic fuel and oxidizer tanks and for pressurizing the ullage space in cryogenic tanks either to provide pressure for direct liquid transfer or simply to provide net positive suction pressure for a transfer pump. Helium frequently is also used as the working fluid in pneumatic control systems. Cold helium has also been used to precool upper-stage, liquid-hydrogen rocket engines prior to launch in order to gain maximum propulsive efficiency during the first few moments of firing (118). Liquid helium and neon are extensively used to cool cryogenic radiation detectors and other specialized instruments used in the space exploration program (141).

Xenon as recently been adopted as a propulsion agent for spacecraft. In satellites, xenon has replaced traditional hypergolic propellants in obit station keeping thrusters. Many high powered communications satellites use this technology. Similarly, xenon has found application in interplanetary probes. The xenon ion propulsion technology has several variations, but essential involves accelerating xenon ions to generate thrust. The xenon ion engines use are as much as ten times as efficient as the fuel-based thrusters they replace. This translates to either longer life or increased satellite payload.

9.8. Medical and Breathing Gases. The main physiological effect of the nonradioactive noble gases is a narcotic one. The so-called inert breathing gases which, although they are chemically unchanged by metabolic processes, exert prominent effects on some cellular functions (142). Of the several schemes for correlating narcotic potency with other gas properties, one of the earliest and still useful schemes is the Meyer-Overton hypothesis. This correlates narcotic

Table 10. **Narcotic Potency and Solubility in Olive Oil of Some Metabolically Inert Gases**[a]

Gas	ED_{50},[b] kPa	Bunsen coefficient at 37°C
cyclopropane	4.6	7.15
dichlorodifluoromethane	26	5.1
ethylene	48	1.28
xenon	52	1.7
nitrous oxide	59	1.6
krypton	182	0.43
sulfur hexaflouride	189	0.25
methane	294	0.28
argon	1,280	0.14
nitrogen	1,820	0.067
helium	>16,500	0.015

[a] Ref. 143.

[b] ED_{50}, narcotic potency, is expressed as the partial pressure of a gas in breathing mixtures required to produce a certain degree of anesthesia in 50% of the test animals.

potency, a gas's solubility in nerve tissue lipids which can be approximated by its solubility in light oils such as olive oil.

The narcotic potency and solubility in olive oil of several metabolically inert gases are listed in Table 10. The narcotic potency, ED_{50}, is expressed as the partial pressure of the gas in breathing mixtures required to produce a certain degree of anesthesia in 50% of the test animals. The solubilities are expressed as Bunsen coefficients, the volume of atmospheric pressure gas dissolved by an equal volume of liquid. The lipid solubility of xenon is about the same as that of nitrous oxide, a commonly used light anesthetic, and its narcotic potency is also about the same. As an anesthetic, xenon has the virtues of reasonable potency, nonflammability, chemical inertness, and easy elimination by the body, but its scarcity and great cost preclude its wide use for this purpose (see Anesthetics). However, there is renewed interest in xenon as an anesthetic agent since it is more cardiostable than traditional anesthetics. For patients with sick hearts, xenon shows reduced risk of operations.

In a related application, xenon has been shown to exhibit neuroprotective properties and can help protect damaged nerve cells from dying. While the application is still under development, there is the potential that it could be used to treat nerve damaging conditions such as strokes or spinal cord injuries.

Xenon is also used as a contrast agent in computed tomography (CT) imaging. This applications has found use mainly in Japan.

The main physiological application of the noble gases comes at the other extreme; because of its small (143) or nonexistant (144) narcotic effect, helium is used to replace nitrogen in breathing mixtures for deep sea divers. Nitrogen in compressed air creates narcosis noticeable at depths below ~40 m and debilitating at ~80 m. Helium–oxygen breathing mixtures have permitted successful open sea dives to 350 m (145) and simulated dives in wet chambers to 490 m and in dry chambers to 610 m (146). In addition, the lower density and viscosity of helium–oxygen mixtures lessens the physical effort required to overcome the high breathing resistance of the heavier compressed gases. However, the much higher sonic velocity in helium mixtures radically changes vocal frequencies, thereby creating communications problems, and the high thermal conductivity of helium increases the rate of body heat loss to the extent that actively heated diving suits and breathing gas preheaters are often necessary (147). Sometimes, neon and neon–helium mixtures are also used in hyperbaric breathing mixtures.

The quantity of breathing gas consumed in deep dives is of both economical and logistical concern; at depths of 300 m, a reasonably active diver requires $\sim 1.8\,\mathrm{m}^3$ ($64\,\mathrm{ft}^3$ at STP) of breathing gas per minute. In closed-cycle breathing systems, of both the self-contained and umbilical types, the helium is recirculated after carbon dioxide is removed and the oxygen replenished (148).

The low breathing resistance of helium–oxygen mixtures is of therapeutic advantage for patients suffering from asthma and other obstructive respiratory difficulties. The helium shows lower resistance to flow than the nitrogen it replaces. The mixtures have also been used for hyperbaric therapy (149).

9.9. Window Insulation. Due to concerns about high energy costs and environmental pollution, argon, krypton and krypton mixtures have begun to be used as a filler gas between multipane windows. The multipane windows are commonly known as inert glass units (IGUs). The gas or gas mixture is inserted into the annular space between the panes, where its higher heat capacity lowers conductive and convective heat losses. When IGUs are installed in building or homes, the improved thermal efficiency results in lower energy costs. With less energy used, the pollution associated with energy production, commonly CO_2, is reduced. In some cases the noble gases are mixed with other gases such as SF_6, which provides sound deadening.

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