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Rare gases in electronics: The nobility of the gases world

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cover story

RARE GASES IN ELECTRONICS
THE NOBILITY OF THE GASES WORLD

Rare gases offer unique properties essential to advanced semiconductor manufacturing.
Linde Electronics explains the role they play in everything from chip making to IoT sensors and beyond. By Sahir Khan (left), Global Product Manager, Linde Electronics and Paul Stockman (right), Head of Market Development, Linde Electronics

Helium tube trailer

RARE – OR NOBLE – GASES, which constitute less than 1 percent of the total air in the earth's atmosphere, play an essential role in the world of electronics manufacturing. These chemical elements make up column 18 of the periodic table, which includes helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn). The term rare denotes that they were first identified as being different from oxygen, while the term noble is an analogy to the inertness of noble metals like gold and platinum.

Chemists group rare gases in the last column of the periodic table because they all have completely filled outer electron shells. This renders them nearly non-reactive and means they exist as gases at ambient conditions, even for the heaviest among them.
Rare gases have unique properties that make them indispensable in electronics manufacturing processes. In this article, we will explore their history, properties and applications, production and supply chain, and market.

History

Sun god, New, Lazy, Hidden, Stranger: the direct translations from the Greek for helium, neon, argon, krypton, and xenon denote the elusiveness of these elements from discovery. Due to their evasive qualities – inert, invisible, gaseous, sparse – the rare gases remained undetected during much of the period of chemical enlightenment of the 18th and 19th centuries. In fact, the location of the first real identification of a rare gas in 1868 was not on the earth at all, but rather from the spectral discharge of helium in the sun.

However, technology quickly enabled a rapid progress in understanding (Figure 1). Building upon earlier scientific and commercial successes with refrigeration, Carl von Linde developed the first apparatus for the liquefaction of air, which was patented in 1895.

While preserving the commercial benefits, Linde also realized the scientific impact of this technology, and distributed early prototypes to major academic centers across Europe. Within 10 years of this technical breakthrough, all five rare gases were isolated and identified, culminating in Nobel Prizes in 1904. Moreover, their discovery was essential to the formulation of the periodic table by Dimitri Mendeleev, and indeed modern atomic theory.

Properties and applications

Properties. The complete, outer electron shells of rare gases are not only an organizing nomenclature for the periodic table, but they also underlie the physical source of key properties associated with these molecules. Essentially similar electronically, rare gases are differentiated among themselves by their mass. Here, we describe four properties important to supporting electronics manufacturing.

- **Inertness:** Foremost among the properties utilized from rare gases is their inertness to chemical reaction. This is why the analogy to noble metals was made by early researchers, noting their lack of oxidation under the most extreme conditions. The complete electron shells mean that these molecules are already at their lowest chemical energy potential, and no reactions with other atoms will improve upon their energy state. Because many of the applications in electronics manufacturing are highly energetic, rare gases are relied upon as an inert medium for conductance of mass, heat, and light.
- **Ionization potential:** Ionization is the removal or addition of electronic charge to an atom or molecule; ionization potential is the energy required to accomplish this charging. Relative to similarly

Linde technology enables discovery

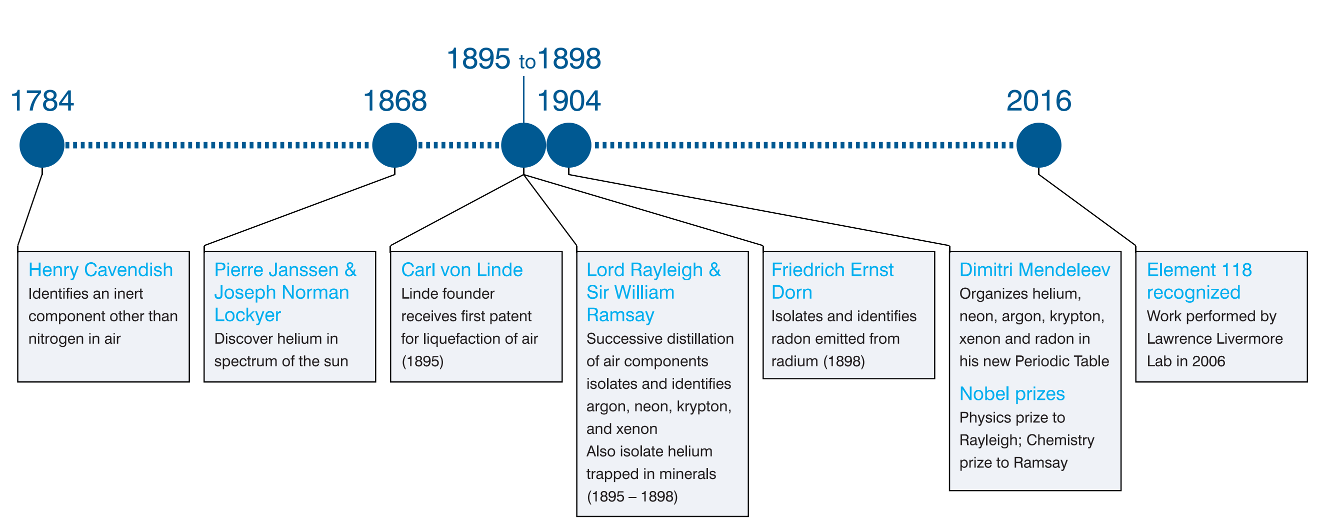


Figure 1. The development of air liquefaction technology by Carl von Linde catalyzed a decade of rare gas discovery, culminating in the organization of the periodic table by Mendeleev and the award of two Nobel Prizes.

massed atoms, rare gases have very high ionization potentials due to their complete electron shells. This allows them to remove or conduct electronic charge efficiently to other atoms and molecules. Helium has the highest ionization potential of any atom or molecule.

- **Thermal conductivity:** Atoms and molecules have different rates at which they conduct heat energy, and this is quantified by their thermal conductivity. Helium, as well as hydrogen, have the highest thermal conductivity among gases, which is due to their low mass. Because of the high-energy reactions of many electronics manufacturing reactions, the combination of high thermal conductivity along with inertness means helium is often used to quickly change the temperature of objects.
- **Mass:** Mass itself is an important property for rare gases. Matching the mass of the rare gas to certain mechanically-enabled applications, again along with their inertness, means the selection of a specific rare gas can optimize outcomes.

Applications. Rare gases are used throughout the wafer substrate and device manufacturing process chains. Here we briefly describe some of the more common applications using rare gases, and show how they are associated with individual rare gases and their properties in Figure 2.

- **Backside wafer cooling:** Helium is often used to control the temperature of wafers and sometimes glass substrates in display manufacturing. This is becoming increasingly important as thermally sensitive, low temperature deposition and etch processes are adopted.
- **Loadlock cooling:** Likewise, helium is used to cool wafers between process steps.
- **Carrier gas:** Helium, and sometimes argon, are used to entrain and transport less volatile chemicals – ordinarily liquids at ambient conditions – into the reaction chamber.
- **Plasma:** Argon, and sometimes helium, are used to support plasmas in deposition and etch processes due to their high ionization potential and inertness.
- **Silicon ingot production:** Nitrogen is reactive to silicon at its melting point of 1414°C, and so argon is used instead to inert the surfaces of the molten silicon and newly formed ingots.
- **Cryogenic cleaning:** Microscopic aerosols of liquid argon have found use to clean delicate, high aspect ratio structures in advanced semiconductor manufacturing.
- **Excimer laser lithography:** Deep UV laser lithography has been used for 20 years in high-volume semiconductor manufacturing to pattern critical layers of devices. Laser gases are mixtures of 98+ percent neon with other rare gases (argon, krypton, and xenon) and halogen (usually fluorine).
- **Sputtering:** Sputtering is the direct removal, or indirect deposition, of material. The process is initiated by the physical impact of gas-phase atoms or molecules upon solid surfaces. By selecting a rare gas of similar mass, sputtering yields can be optimized.
- **Etch:** Rare gases are used to mediate etch reactions. Xenon is used in certain high aspect ratio etch applications for its combination of ionization potential and chemical inertness to adjust charge distributions in the etch reaction.

Production and supply

Cryogenic Distillation. Production and supply of rare gases are enabled by the same cryogenic distillation separation of air components pioneered by Carl von Linde more than 130 years ago.

The relative abundance of the components in air (Figure 3) and boiling points (Figure 4) indicate the cost to produce and availability to supply these critical materials to the typical 99.999+ percent purity.

Argon
Argon is the fourth most abundant gas in the earth's atmosphere. It is produced in air separation units (ASUs) alongside oxygen and nitrogen by means of secondary distillation of the liquid oxygen rather than from the primary distillation of air. Because the boiling point of argon is between that of nitrogen and oxygen, an argon-rich mixture is taken from a tray near the center of the distillation column and is further cryogenically separated. It can also be recovered from ammonia plant purge gas streams, which also process very large flows of air as an initial feedstock for nitrogen.

Neon, Krypton, and Xenon
Neon, krypton, and xenon are similarly obtained as by-products from the production of nitrogen and oxygen. Because the concentrations in air are miniscule, commercial quantities of crude products are obtained from only the largest ASUs with huge air intakes: on the order of at least 1,000 tons per day (tpd) oxygen capacity are needed. Neon has a much lower boiling point than nitrogen and oxygen and thus passes through the nitrogen distillation column unliquefied. This "light" stream is compressed and sent to secondary sites for further purification and packaging. Krypton and xenon conversely have much higher boiling points and are rejected from the oxygen distillation column as "heavy" waste. They are pre-purified at site to remove most of the oxygen before similarly being sent to secondary sites for further purification – including separation from each other – and packaging.

Helium
Helium is the most abundant element found in the universe after hydrogen, but it is relatively rare on earth. Helium is formed on earth as a result of the radioactive decay of thorium and uranium in the crust. It rises through geological fissures and accumulates in the same rock formations as natural gas. However, only certain deposits have concentrations high enough to be commercially viable, but which are less costly than distillation of air.

Commercial production of helium began in the United States as a strategic material spurred by the military applications for observation blimps during World War I. The primary commercial source for much of the 20th century was the Hugoton gas basin spanning parts of Kansas, Oklahoma, and Texas. During this period, the US government continued to treat the material as strategic, and excess crude material obtained as the by-product of natural gas extraction was stored by returning it to depleted reservoirs of permeable rock. Known as the Federal Helium Reserve and managed by the Bureau of Land Management (BLM) the reserve is in the process of being sold off under the Helium Stewardship Act of 2013 and this erstwhile primary supply will be tapered to negligible commercial impact in the near future. Meanwhile, significant new sources have been developed over the past few decades across the globe. The potential development of large sources in Siberia promises to continue to meet growing global demand.

Recovery
Due to their inert property, rare gases are not consumed, either by chemical change or incorporation into the finished product, during electronics manufacturing. Consequently, they are available in the waste streams from fabs, albeit highly diluted and contaminated. The technology to recover

Applications and Properties

	Gases					Properties			
Applications	Helium	Argon	Neon	Krypton	Xenon	Inert	Ionization potential	Heat coefficient	Mass
Backside wafer cooling	●					●		●	
Load lock cooling	●					●		●	
Carrier gas	●	●				●			
Plasma	●	●				●	●		
Silicon ingot production		●				●			
Cryogenic cleaning		●				●			
Excimer lasers		●	●	●	●	●	●		
Sputtering		●		●	●	●			●
Etch					●		●		

Figure 2. Specific and often extreme properties of rare gases result in their roles for essential electronics applications.

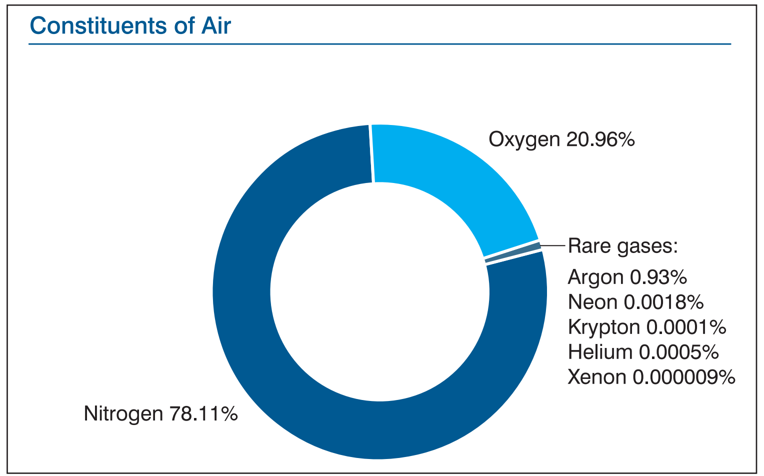


Figure 3. Rare gases are a small part of the atmosphere.

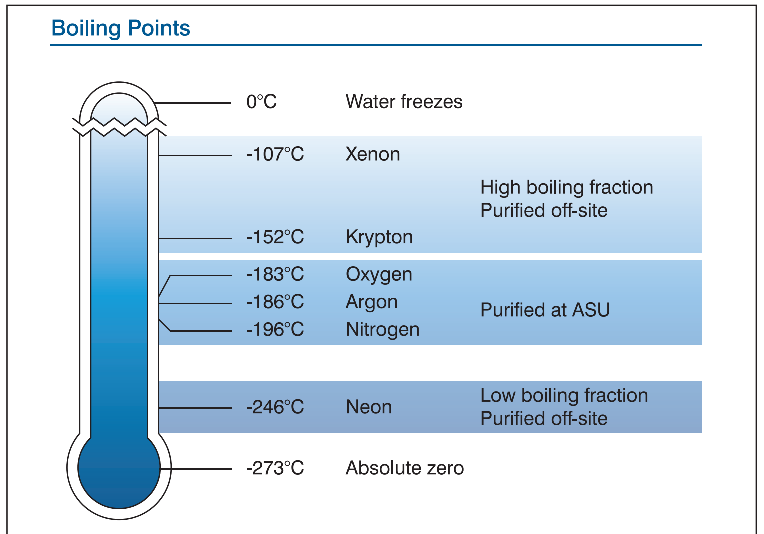
these materials is straightforward, with the potential to recycle them for electronics or other applications. However, as with most recovery processes, the choice to recover vs. supply with new material is made on the relative costs of the whole supply chain. Only the very largest use applications are candidates for commercially successful recovery.

Supply Modes. Rare gases are available in a variety of gas and liquid packaging, as indicated in Figure 5. These span from lecture bottle cylinders holding a few liters of gas to liquid bulk trucks for land and ISO containers for sea shipment of millions of gas-equivalent liters of product. Like most materials, the commercially viable transport cost is directly related to the value of the material (Figure 6). Because most rare gases are truly scarce, they are commonly distributed globally and generally independent of the geographic location of the source. The exception is argon, which is relatively inexpensive, and is produced in many geographies at large ASUs. However, it can be shipped regionally as supply imbalances dictate.

Figure 4. Extracting rare gases requires cryogenic distillation of large quantities of air.

Market

The demand for rare gases has grown substantially in the past few decades on the back of new applications both for electronics and non-electronics markets. Moreover, while the overall demand for these materials has experienced a more-or-less smooth upward trend, the underlying application basis has sometimes changed dramatically. For example, the development and rapid adoption of LED lighting has quickly eroded the market for halogen lighting and display signage. Likewise, the market for plasma displays as a successor to cathode ray tube televisions was short-lived and eclipsed by the introduction of LCD technology. Below, we take a brief look at the electronics market demand, as well as significant non-electronics applications. These market shares are summarized in Figure 7.



Helium

- **Electronics:** Electronics usage, which represented less than 1 percent of total global demand for helium, has grown exponentially to constitute more than 15 percent of the market demand today. The total demand for helium for a single fab can now exceed 200,000 m³ per year.
- **Non-electronics:** Non-electronics applications include cooling in metal production and adoption of MRI scanners, whose superconducting magnets require liquid helium as a refrigerant. Fiber optic manufacture can also benefit from using helium as a coolant to speed the manufacturing process.

Neon

- **Electronics:** Dominated by DUV laser lithography, usage continues to out-scale wafer start growth as the complexity of leading-edge chip designs drives adoption of multi-patterning lithographic techniques. Laser annealing and lift-off for new display technologies will further accelerate demand.
- **Non-electronics:** Dissolution of signage applications has quickly reduced the non-electronics demand and ceded supply availability to electronics.

Argon

- **Electronics:** Argon is the primary inert gas used in the fab due to its relative inexpensive cost to supply. Usage continues to trend with process complexity. Geographic supply imbalances occur sometimes when large wafer or ingot fabs are built in regions lacking in ASU-intensive industries like steel and chemical production.
- **Non-electronics:** Usage is widely varied for inerting of high-temperature material processing, like the manufacture of stainless steel and as a plasma gas for welding.

Krypton

- **Electronics:** Usage in electronics is co-reactant in DUV excimer lasers and sputtering account for the relatively small electronics demand.
- **Non-electronics:** In these applications, krypton is used as an insulator between panes of glass.

Xenon

- **Electronics:** Long used in R&D as an etch enhancer for high-aspect ratio etch, xenon is finding high-volume commercial adoption for such etch applications in new 3D semiconductor structures.
- **Non-electronics:** LED adoption has reduced xenon use for halogen lighting to one third its former demand in the span of the last three years. However, its use as the propellant for space satellites in non-military launches is growing rapidly, which is replacing lighting as the demand driver.

Packaging

	Gas			Liquid		
	Cylinder	MCP (multi-cylinder pack)	Tube trailer	Dewar	ISO container	Bulk truck
Helium	●	●	●	●	●	
Argon	●		●			
Neon	●	●		●	●	●
Krypton	●					
Xenon	●					

Figure 5. Rare gases are supplied in a wide range of gas and liquid packages.

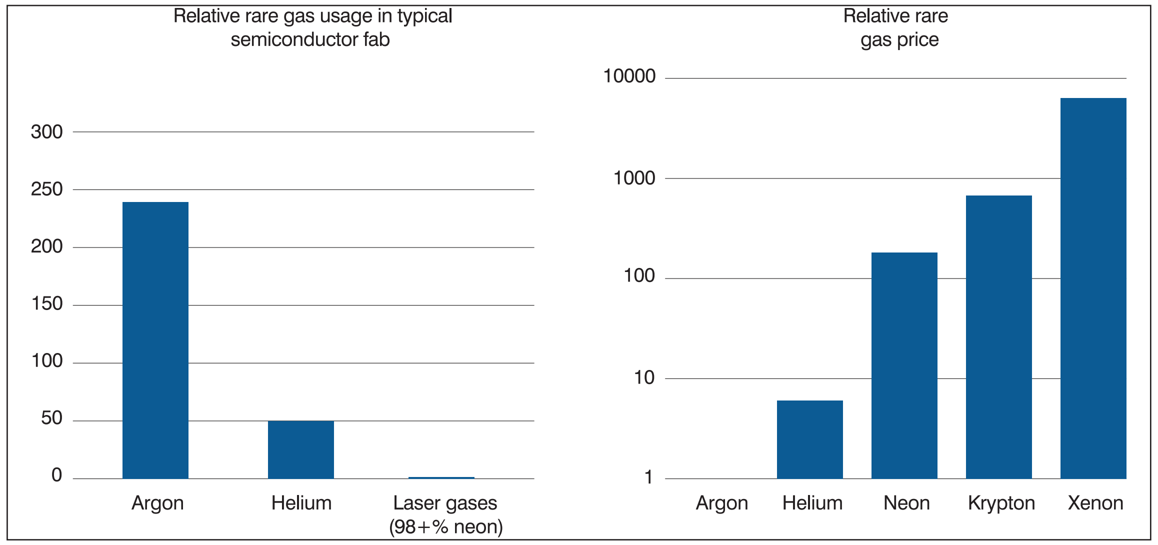


Figure 6. Rare gas usage and price are inversely proportional.

Conclusion

Long invisible to us although they surround us in the air, rare gases were quickly discovered after the enabling invention of air liquefaction by Carl von Linde. The technology to produce these molecules is advanced and the sourcing and production of rare gases is a specialist niche field. Scaling of ever larger ASU plants have made supply of these gases commercially viable, along with exploration and development for geological sources of helium.

From the beginning of semiconductor processing, rare gases have been important for the inerting properties they provide. As the industry has developed in technical complexity, rare gases have filled an ever widening matrix of essential applications. And now, electronics applications form a significant share of the market demand for all of these with the exception of argon.

Linde is the leading supplier of the technology to extract these needed gases. Using the world's largest portfolio of its own production plants as well as contracts with third-party producers, Linde manages the full supply chain of rare gases to meet the volume and quality demands of its electronics customers. Linde anticipates its customers' developing requirements by continuing to be the innovator in its field.

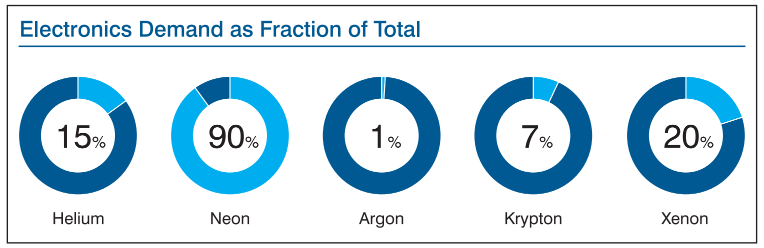


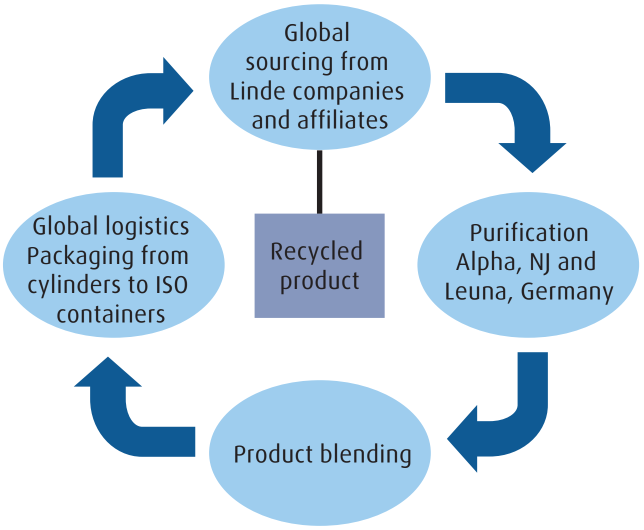
Figure 7. Electronics application demand makes up widely varying fractions of the total market for each of the rare gases.

Leading the market with end-to-end rare gases supply chain

Investing in multiple-site rare gas production, blending, and purification facilities to assure long-term and secure supply worldwide

Linde is the only rare gases provider that can provide a robust supply chain including internal production and external partners, cryogenic production and purification technology, proprietary IP for the blending and analysis of laser gas mixes, in-house quality control capabilities, plant design and production, plus this product line:

- → Helium – Most diverse portfolio of helium-producing assets
- → Argon – Production off-site, delivery and on-site storage as liquid, and distribution on demand
- → Neon, krypton, and xenon – Air separation units, purification, blending, and mixing
- → Xenon difluoride – Global distributor and direct air shipment
- → Xenon and neon recovery – On-site recovery and off-site reclamation, purification, and analysis
- → Complete portfolio of laser gases – ArF, KrF, Kr/Ne, Ar/Xe/Ne, and HCl and BCl_3 mixes



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