Leo Dana: Cryogenic science and technology

Following one academic and industrial career takes us on a tour of some of this century's most scientifically interesting and economically important discoveries in low-temperature physics, including helium's lambda transition and superinsulation.

Russell J. Donnelly

Progress in low-temperature physics is so rapid today that it is difficult to realize that the field scarcely existed 100 years ago. Leo Isadore Dana is not a familiar name to many physicists, but his contributions during the years 1920–64, a period of many important advances in cryogenics, span a remarkable range of phenomena in low-temperature physics and technology. This article recalls some of the important projects, from basic research on liquid helium to a wide range of activities in cryogenic and other technology.

Dana had that instinct for what is important that is the hallmark of all great scientists. He demonstrated this in a brief stay at Leiden University in Holland in 1922–23, when he made two of the key measurements that led to the identification of the λ transition in liquid helium, surely one of the greatest discoveries of 20th-century physics. In 1923 Dana joined the Linde Air Products Company, a division of the Union Carbide and Carbon Corporation, where he spent his entire career. His influence on cryogenic technology (such as the superinsulation used in the truck shown in figure 1) was remarkable and is only beginning to be appreciated.

My interest in Dana began while I was preparing a review article on the specific heat of liquid helium. The first reference was the pioneering measurement by Dana and Heike Kamerlingh Onnes. Through mutual acquaintances I was able to contact Dana, who very kindly prepared for me a memoir of his experiences at Leiden University. The box on page 42 contains excerpts. I realized that this memoir told only a small part of Dana's story, and I began to search for publications and further information on Dana's career. Linde provided both and put me in contact with Arthur W. Francis, who had worked for Dana. Francis contributed a brief description of Dana's industrial career. The result is a small book recently published by Union Carbide.[1]

Dana was born in 1895 to Russian immigrant parents. He attended Boston English High School and then MIT, where he received a bachelor's degree in industrial physics. Dana did research on high-temperature refractories for two years at the US Bureau of Standards in Washington, DC, and then attended graduate school at Harvard. In 1922 he completed his dissertation, *The Latent Heat of Vaporization of Liquid Oxygen–Nitrogen Mixtures*. He then went off to Leiden for ten months on a fellowship.

Five years after returning to the United States and taking the job at Linde, in Buffalo, New York, Dana became superintendent of research at the Linde Laboratory. By 1931 he was manager of research and engineering development. In 1942 Dana transferred to New York City, and in 1953 he became vice president of technology for Linde, a position he held until his retirement in 1964. Dana now resides in Boca Raton, Florida.

Liquid oxygen industry

The methods used today to liquefy gases were not discovered until late 1877, when Louis Cailletet in France and Raoul Pictet in Switzerland discovered the expansion and cascade methods of producing liquid air. The liquefaction of a sample of oxygen boiling in a test tube (as distinct from the observation of droplets of liquid) was achieved in 1883 at the University of Cracow by Zygmunt von Wroblewski and Karol Olszewski. The Joule–Thomson effect—the cooling of expanding non-ideal gases, discovered in the mid-1800s—eventually proved to be the most important method for producing low temperatures and liquefying gases.

In 1895 Karl von Linde in Germany patented the process for separating oxygen from liquid air. Von Linde had founded the Gesellschaft für Linde Eismaschinen to manufacture ice machines; later the firm turned to producing oxygen by liquefying air and distilling the resulting liquid. Between 1895 and 1906 oxygen-producing plants were found only in Europe. In 1906 Linde British Refrigeration Company, the British agent for von Linde's German company, built a plant in Birmingham, England, with equipment from Germany. Shortly after the plant opened, the British Oxygen Company was formed and Linde British Refrigeration

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Truck with a tank capable of holding 10 000 gallons of liquid hydrogen or liquid helium for extended periods without appreciable loss. Superinsulation and liquid nitrogen jacketing limit losses to 50 gallons per day. (Photo courtesy of the Linde division of Union Carbide Corporation.) Figure 1

ceased producing liquid oxygen. Timothy Bell Lightfoot, the managing director of Linde British Refrigeration, was a director of the new British Oxygen Company, and got British Oxygen to bring the Linde process to America. In 1906 von Linde asked Cecil Lightfoot, son of Timothy Bell Lightfoot, to help establish a Linde oxygen plant in America. They chose Buffalo because it was centrally located with respect to major industrial centers and because it was near Niagara Falls power. The Linde Air Products Company was incorporated on 24 January 1907—the beginning of a major new industry in the United States.

At first Germany supplied the technology and equipment for liquefaction and separation. The American company gradually improved the technology and built a shop to produce the equipment in Buffalo. After 1923, when Dana was hired, the laboratory created and introduced new designs for the parts that made up the liquefaction and separation units, hiring increasing numbers of engineers to do the research and development work. Linde's subsequent achievements in the development of thermal insulation demonstrate the effectiveness of this approach. The description of these achievements given below draws upon Francis's recollections of the work.[1]

Thermal insulation

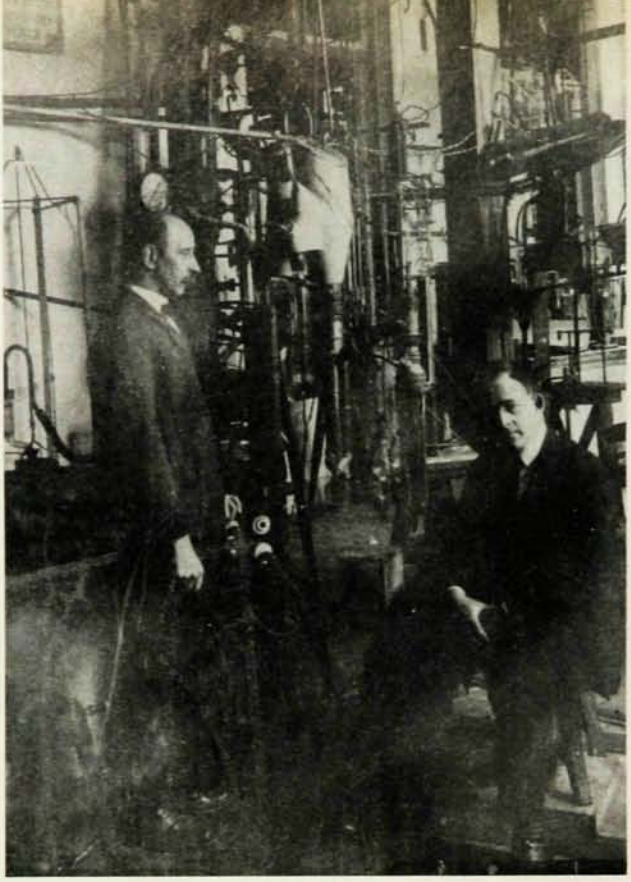
Oxygen is produced by distilling liquid air. Gaseous oxygen, compressed to 150 atmospheres, is marketed in the heavy-walled steel cylinders that are familiar sights in research laboratories and welding shops. These cylinders, however, are not efficient for transporting large quantities of gas. Containers of liquid oxygen, on the other hand, contain five times as much oxygen as the same weight of cylinders. In the 1920s the industry began to market liquid oxygen to reduce distribution costs. Progress was limited because insulation at that time was not efficient and glass Dewar flasks were impractical for commercial use. The first attempts to build liquid containers used insulation made from fibers such as rock wool and powders such as diatomaceous earth. These insulators had proven satisfactory for cold storage plants at the relatively high temperature of 253 K. Liquid oxygen, however, must be maintained at 87 K, and these old-style insulators limited shipping time to a few hours.

The transfer of heat between two bodies at different temperatures takes place by conduction, convection and radiation. Laboratory Dewar flasks are double-walled containers with an evacuated inner space. Heat cannot cross the evacuated space by either conduction or convection. Low-emissivity surfaces such as silver reduce the radiation. Glass Dewars require a vacuum of about 10^{-5} torr, but this is impractical with industrial-scale metal tankage.

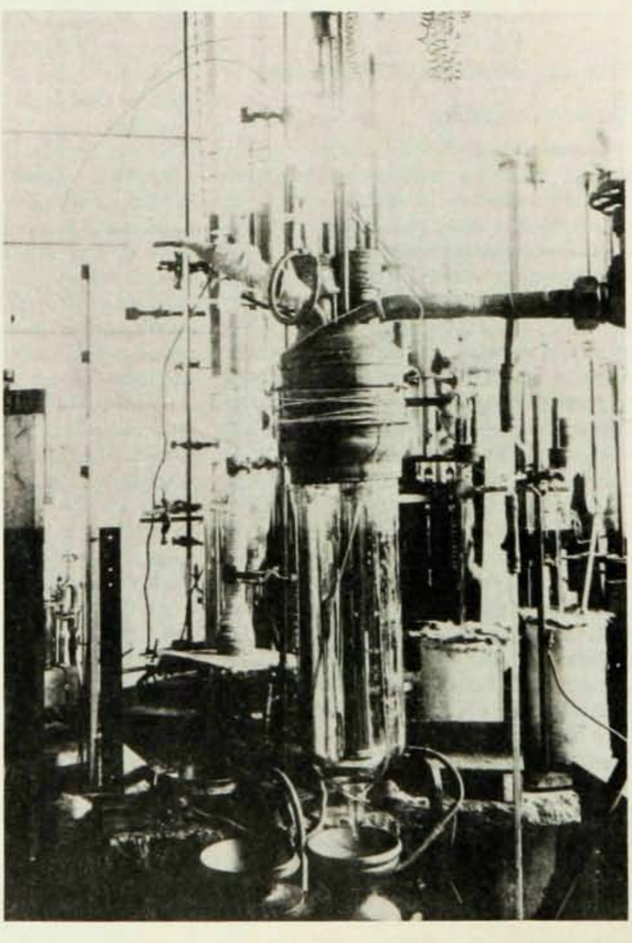
Dana and his associates determined that heat transfer is exceptionally low when the space is evacuated to a relatively modest vacuum and filled with a fine powder. Radiation is reduced without the use of low-emissivity surfaces, and the increase in solid conduction due to the powder is surprisingly small. Dana's "powder in vacuum" insulation, which is one hundred times better than rock wool, has become a worldwide standard in the air separation industry. Using Dana's insulation technique, air separators in the United States distribute seven million gallons of liquefied gases every day to the steel, welding and chemical industries.

Developments in powder-in-vacuum insulation continued through the 1930s and 1940s, but Dana realized that further commercial development required a major advance. He established a laboratory for low-temperature engineering research at the Linde division. The laboratory's first objective was to do the fundamental research necessary to develop thermal insulation ten times better than powder in vacuum.

The lab undertook experiments to



Leo Dana (right) and G. J. Flim, head technical assistant, in the low-temperature laboratory at Leiden University, 1923. (Photo courtesy of Dana.) Figure 2



Cryostat for liquid helium containing the calorimeter that Dana used at Leiden. The cryostat is surrounded by concentric Dewar flasks that held liquid hydrogen and liquid air for thermal isolation. Figure 3

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determine for various materials what portion of the overall heat leak is due to solid conduction and what portion to radiation. Perlite and other materials that performed well in the conventional powder-in-vacuum technique transferred nearly all heat by solid conduction. Materials that gave a higher overall heat leak were found to have very little solid conduction but surprisingly high radiative heat transfer. Although these materials are opaque to visible light they are nearly transparent to infrared radiation. Further experiments demonstrated that opacifying agents could suppress radiation without significantly increasing solid conduction. Following this strategy Dana's lab developed a class of "superinsulation," which is up to one hundred times better than the best powder in vacuum. The superinsulation shown in figure 6 consists of nine layers of thin aluminized Mylar sheets held apart by nylon netting.

Superinsulation plays a vital role in every technological application of liquid helium. Recently developed scientific uses of liquid helium require much greater quantities than previously envisioned. The new uses include cooling superconducting magnets in accelerators and in magnetic resonance imaging devices, and cooling radiation detectors and SQUIDS (for a discussion of SQUIDS, see John Clarke's article, PHYSICS TODAY, March 1986, page 36). Helium liquefied in Kansas is shipped in bulk to Europe, Brazil, Japan and Australia. Ocean shipments taking up to five weeks arrive without appreciable loss. Suppliers send containers of 30–500-liter capacity by air freight to all parts of the world. For land shipment, they place larger containers on trucks, as figure 1 shows. Francis has noted: "The effectiveness of these containers is astounding. If fresh-brewed coffee could be insulated as well, it would remain hot enough to drink throughout a normal lifetime (70 years)."

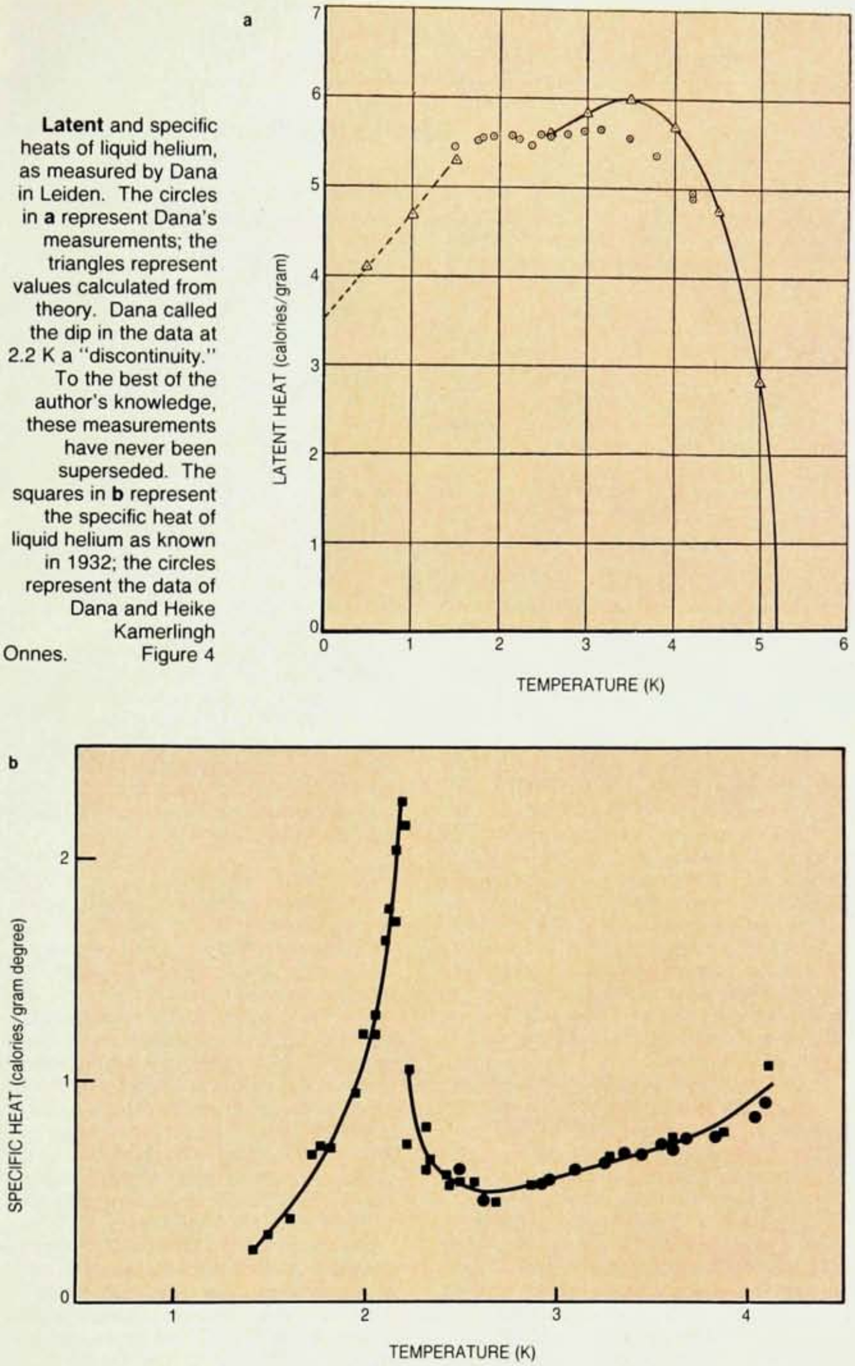
Improvements in thermal insulation represent only one facet of Dana's achievements at Union Carbide. Dana and his associates also initiated the use of pumps for low-temperature liquids. Turbine-type pumps can move cryogenic liquids at high flow rates to and from low-pressure tanks. In more highly developed form these pumps are the heart of liquid-fuel rocket engines.

Molecular sieves

Linde was continually seeking new methods for separating gases. Among the possible alternatives to the traditional distillation method was the use of materials that have different absorption capacities for different molecules. Robert M. Milton, a member of Dana's laboratory, suggested this technique. Zeolites are an appropriate material for this method because they can be produced with controlled molecular architectures. The petroleum and chemical industries use zeolites as catalysts and absorbents, and zeolite production is now a large business with several plants in the United States and overseas.

Zeolites also play an important role in laboratory low-temperature physics. Small amounts of zeolite 5A can be used to absorb residual gases, and larger amounts in thermal contact with liquid helium make highly efficient absorption pumps for portable cryostats such as the one shown in figure 6. The operation of this cryostat, developed at the University of Oregon by Ira Nolt and James Radostitz, depends on a container holding about 100 grams of zeolite 5A in thermal contact with the main helium bath at 4.2 K through a concentric vacuum space connected to a smaller zeolite pump. Helium-3 contained in a storage can is condensed into the evaporation pot connected to the experiment of interest and is cooled by exposure to the zeolite, which pumps by simply absorbing helium vapor. The He^3 cools to 0.35 K, and the zeolite pump can maintain this temperature for more than 50 hours. After the pump is saturated with He^3, one can regenerate it by using the second small pump, which contains about 10 grams of zeolite, to evacuate the vacuum space about the larger pump. One isolates the large pump and warms it to about 50 K, which expells 95% of the He^3. One then warms the small pump, driving gas into the vacuum space, and pumping can begin again. The large pump has a zeolite-controlled heat switch and the whole operation proceeds without moving parts.

This technology allows one to put cryostats on telescopes, fly them on balloons and use them on rotating tables—wherever one needs freedom from mechanical pumps.



Latent and specific heats of liquid helium, as measured by Dana in Leiden. The circles in **a** represent Dana's measurements; the triangles represent values calculated from theory. Dana called the dip in the data at 2.2 K a "discontinuity." To the best of the author's knowledge, these measurements have never been superseded. The squares in **b** represent the specific heat of liquid helium as known in 1932; the circles represent the data of Dana and Heike Kamerlingh Onnes. Figure 4

Research outside cryogenics

It is worth recalling the amazing variety of projects Dana worked on during an active career that spanned almost half the history of low-temperature physics.

Under Dana's direction the Linde division of Union Carbide obtained funding for research outside cryogenics. Dana's philosophy in picking research projects had two components: to explore freely new ideas to determine whether or not they are commercially feasible, and to develop "synergy," which Dana defined as the use by one Union Carbide unit of new materials, techniques or skills available in another unit. The three projects described below are examples of important work outside cryogenics in which Dana played a role.

Antifreeze. The first project outside Linde's specialty involved antifreeze for automobile engines. Ethyl alcohol had been the universal coolant for liquid-cooled engines. Water solutions of ethyl alcohol had sufficiently low freezing points, but the boiling point of the alcohol was lower than that of water, resulting in rapid evaporation of the alcohol and possible damage to the engine due to overheating.

The Chemicals Company of Union Carbide had begun to manufacture ethylene glycol, and because its boiling

Life in the Kamerlingh Onnes lab

In the early 1920s Leo Dana went to Leiden University for a brief but fruitful stay at the lab of Heike Kamerlingh Onnes. Here Dana describes his experiences at that famed research center.

Having done low-temperature research at Harvard University for my doctoral thesis, completed in June 1922, I felt a great desire to continue research in this field after graduation. I applied for a Sheldon traveling fellowship and was fortunate to receive one. No strings were attached to this fellowship other than to do research as a postgraduate fellow in a university, preferably a foreign one. Because my thesis covered measurements of the latent heat of liquid oxygen–nitrogen mixtures, I was anxious to continue similar research on liquid helium with Heike Kamerlingh Onnes, director of the cryogenics laboratory at Leiden University in Holland. Leiden University was the center of research in this field, and was also the gathering center for lectures and research by the leading physicists of Europe.

Arriving in September, I found the laboratory in disarray owing to the death of Jan Pieter Kuenen, who had been named to succeed Kamerlingh Onnes as director. I was not able to meet Kamerlingh Onnes because he was reportedly ailing and upset over Kuenen's death, and had not been to the laboratory. After a few weeks I wrote to Kamerlingh Onnes stating that I thought he would agree that Harvard University would be disappointed if I were not able to do some original research during my stay at Leiden.

In a few days I received a phone call asking me to visit him at his home. He lived in a beautiful house located on a broad canal, and stepping inside, it was evident he was a wealthy man. I was ushered into his study, furnished with antique furniture, oriental rugs, and paintings; looking out the window one saw the lovely scenery of the Dutch countryside. Kamerlingh Onnes was dressed in a fancy velvet gown—the typical man of means.

After a few pleasantries, I told him how I felt about doing original work, and he asked me what I would like to do. I stated that I wanted to measure the specific and latent heats of liquid helium over a range of temperatures. Without hesitation, he said, "Go ahead and do the job." In parting, he gave me a bit of advice: "If you ever see a ripe plum on a tree, reach up and grab it." Unfortunately, I haven't always followed his good advice.

Kamerlingh Onnes's consent opened wide the doors in the laboratory, and subsequently I had free rein to do or have done almost anything to accomplish my objective. This was possible not only because of the approval of the boss, but also—in fact, mainly—because of the unique organization that Kamerlingh Onnes had created. As far as I know this was the greatest and most productive low-temperature research laboratory ever built and organized.

One of Kamerlingh Onnes's great achievements was to create two training schools associated with the laboratory—one for mechanics and machinists and the other for glassblowers. This allowed me to obtain within a few months the apparatus (figure 2) required for specific and latent heat measurements of liquid helium and to complete the research within my ten-month stay. It would have been impossible to accomplish this so quickly anywhere else in the world. Another reason Leiden represented opportunity was that high equipment and operating costs limited the number of institutions that could afford liquid helium facilities. Years later this situation changed when Samuel Collins of MIT developed a simple helium expansion engine with nitrogen precooling, eliminating the need for liquid hydrogen. This, together with the ready availability of liquid nitrogen and gaseous helium, resulted in a drastic reduction of costs and led to the proliferation of liquid helium research facilities throughout the world.

The measurements

It took a whole day, from 7 am to 7 pm, to make a measurement on the thermal properties of liquid helium. The time was required to produce sufficient liquid air, hydrogen and helium and to conserve the gases that evaporated due to conduction, radiation and the vacuum pumping done to get temperatures below the normal boiling point of liquid helium. (See figure 3.) In keeping the laboratory assistants working overtime without pay, I encountered a small labor problem. They protested some about postponing their dinner hour. I solved the difficulty by providing tea and pastries from the local bakery.

We completed the latent heat measurements first, and then the specific heat measurements. The results are shown in figure 4. The latter were completed in July, shortly before I left. The break that appeared in the plot of latent heat as a function of temperature—I described it as a discontinuity—was indeed a startling phenomenon and unknown previously except as a local maximum in the density curve. Much to my regret, I was unable to delve further into this phenomenon because I ran out of funds to extend my stay at Leiden. Several years later, as research in liquid helium expanded, it was found that the break in the latent heat curve was indeed a phase change between two different forms of helium, labeled I and II.

As I recall, neither Kamerlingh Onnes nor members of the scientific staff showed any interest in the data, except perhaps Claude Crommelin. I left Leiden before writing my two papers on the results, but I sent them to Leiden within two months. As usual, it took some time before they appeared in *Communications from the Physical Laboratory of the University of Leiden*, where most of the research there was first published. They also were published in 1926, three years after completion, in the *Proceedings of the Royal Academy, Amsterdam*.

It is worthwhile recalling the academic atmosphere at Leiden during my time there. (Figure 5 recalls some of the humor.) Leiden was a mecca for physicists and mathematicians from all over the world. Hendrik A. Lorentz gave lectures on relativity theory, which I attended. He was a fine lecturer and an imposing gentleman, always taking an interest in welcoming foreigners to his class. Most important were Albert Einstein's lectures on problems related to his theory of relativity. Not only was he a great communicator, but he had a penchant for involving his listeners as participants in the actual experiments and situations he described.

One of the problems he posed to the class dealt with gravity: Suppose that the listener is in an elevator at the top of a high shaft, holding a lantern enclosing a burning candle, and that the elevator is allowed to fall freely in the shaft without friction. Assume that the lantern contains enough air to support combustion of the candle for a number of minutes and that no artificial drafts, as through the small holes in the lantern, affect the burning. Question: During the free fall would the candle be snuffed out or continue to burn? Answer: The candle would go out. The reason is that while the lantern is stationary, the hot gases of combustion tend to rise, bringing in fresh air with oxygen. This circulation is produced by the falling of fresh air to fill the vacuum created by the rising hot air. In the free fall of the lantern, the fresh air will not fall by gravity and the candle will be snuffed out. Einstein, a great teacher, often lectured by posing problems to his audience and then discussing the solution.

Petr Kapitsa, the Russian low-temperature physicist, gave a series of lectures on his research, and Niels Bohr also discussed his exciting new theories in atomic research.

Paul Ehrenfest, who was head of the Institute of Theoretical Physics and Mathematics at Leiden, took a very active part in the scientific life at Leiden. He organized seminars among graduate students and by visiting scientists. He was a dynamic and gregarious man who served as a catalyst in the give and take of discussion and in promoting contacts between individuals. At his request, I talked on Percy Bridgman's work at Harvard University on high-pressure solid-state theories and experiments. I spoke in Dutch, and of course had some difficulties with scientific Dutch, but Ehrenfest kindly came to my rescue.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Cartoons on the laboratory wall at Leiden, drawn for the celebration of the laboratory's 50th anniversary in 1923. Top: The race to absolute zero. Bottom: Wolves as "a few obstacles on the way to absolute zero." Figure 5

point is greater than that of water and because the freezing point of an ethylene glycol–water solution is sufficiently low, it appeared possible to use the solution in automobile radiators. The product was named Prestone Antifreeze, and it had good initial sales. However, after one winter's use, trouble developed. Serious rust deposits formed in radiators, causing clogging and overheating, and the formation of acid destroyed pump impellers.

Union Carbide transferred to Linde Laboratories responsibility for the development and improvement of the product because the problem involved mechanical engineering as well as chemical research.

Linde geared up its facilities to include a dynamometer laboratory with a large number of stationary engines operating around the clock, testing modified antifreeze solutions. An organic chemistry group provided ideas for using alkaline organic chemicals manufactured by the Chemicals Company to retard acid formation in the solutions. Linde also tested the experimental modifications of Prestone in a fleet of automobiles driven by salesmen for thousands of miles in hot and cold weather.

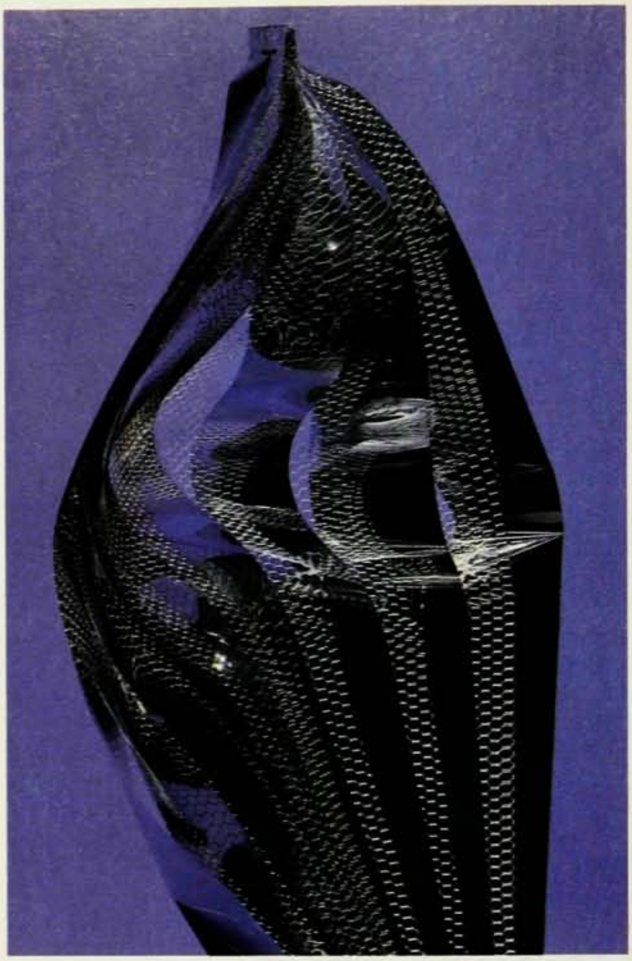
Linde's research on the product was very successful, and together with improvements undertaken by others in the following years, made Prestone the dominant antifreeze in the market.

Polyethylene. In the 1930s Dana noticed a patent issued to Imperial Chemical Industries, the British company, for a process in which batches of ethylene gas at very high pressures would polymerize into a waxlike solid. The patent did not indicate any use for the solid. Because ethylene was the principal building block for chemicals being researched by the newly formed Carbide and Carbon Chemical Corporation, the laboratory decided to look into the matter to see if the process could be made to operate continuously instead of running in batches in a high-pressure autoclave. Linde had been experimenting on processes to produce diamonds at very high pressures, and in doing so had developed a unique high-pressure pump that operated continuously at pressures over 100 000 lbs/in^2 for gases or liquids. The pump was ideal for continuously polymerizing high-pressure ethylene gas. Linde scientists built a small pilot plant and found that they could produce solid polyethylenes of various molecular weights in a simple high-pressure heated pipe; they proceeded to make many samples for testing.

Shortly thereafter, Dana discovered from the manager of Union Carbide's plastics division that duPont had a license under the Imperial Chemical Industries patent and was producing batches of low-dielectric-loss polyethylene for electrical insulation at high frequencies. Great Britain badly needed large quantities for their airplane radars. Given the urgency of wartime, the Linde staff designed and built a pilot plant to produce the required polyethylene. After the war, Union Carbide became the largest producer of this most widely used plastic material.

Uranium. In a recent letter to me, Dana discussed a little-known aspect of the Manhattan Project. I quote from the letter, which bears on the beginnings of Union Carbide's involvement in the Oak Ridge National Laboratory, which it operated from 1942 to 1984:

> In view of the availability of a new laboratory at Linde and our expanding field of research, we decided to examine the possibility of research in inorganic chemicals to broaden the present organic base.



Superinsulation and cryostat. Left: Superinsulation fabricated at the University of Oregon. It consists of nine sheets of aluminized Mylar separated by nylon netting. Right: Jim Radostitz, a senior research associate in the University of Oregon physics department, inserts a roll of superinsulation into a portable helium cryostat used to cool an infrared bolometer detector. The liquid helium is cooled by pumping with an absorption pump consisting of zeolite 5A. The absorption pump is cooled by thermal contact with liquid helium in the main container of the cryostat. Figure 6

J. A. Rafferty, the president of the Chemicals Company, was my mentor and suggested the idea. As a first step, since Carbide was in the metallurgical alloy business, we decided to survey what materials might be available and suitable for study. We looked for waste materials that might be lying around in mines or factories. A vanadium mine existed in Uravan, southwestern Colorado, which produced vanadium oxide from ores containing vanadium and uranium oxides. The vanadium oxide was used to make ferro-vanadium, which in turn was an alloy employed in the electric furnace production of vanadium steels used in automobile axles and other uses. The impure uranium oxide discarded from the ores was dumped in large quantities in tailing piles.

I visited the mine at Uravan and found that the tailings had large quantities of uranium oxide and were suitable for treatment. These tailings were shipped to Tonawanda, New York, and in due course a purification process was worked out. A large pilot plant was built which successfully produced yellow cake, U_3O_8.

It took courage to do this since no real market existed for U_3O_8. Small quantities were employed for producing yellow color on ceramics and for photography. Also the metal had one of the highest densities and found uses in special apparatus.

While the market research was going on, we had not known that the fission of uranium had recently been accomplished in European university laboratories and that the Manhattan District had been organized to produce the atom bomb.

Before long, General [Leslie] Groves visited our yellow cake plant and the decision was made to move it to another area, where further processing could secretly be undertaken to produce uranium hexafluoride needed in the diffusion process to make fissionable uranium.

It is believed our yellow cake process led to further consideration by General Groves to get Union Carbide into the development of Oak Ridge to produce fissionable uranium.

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I am grateful to Leo Dana and Arthur Francis for providing information for this article. I thank the Linde division of Union Carbide Corporation for helping make the article possible.

Reference

1. R. J. Donnelly, A. W. Francis, eds., *Cryogenic Science and Technology: Contributions of Leo I. Dana*, publication no. L-6080, Communications Dept., Union Carbide Corporation, Danbury, Conn. 06817 (1985). □