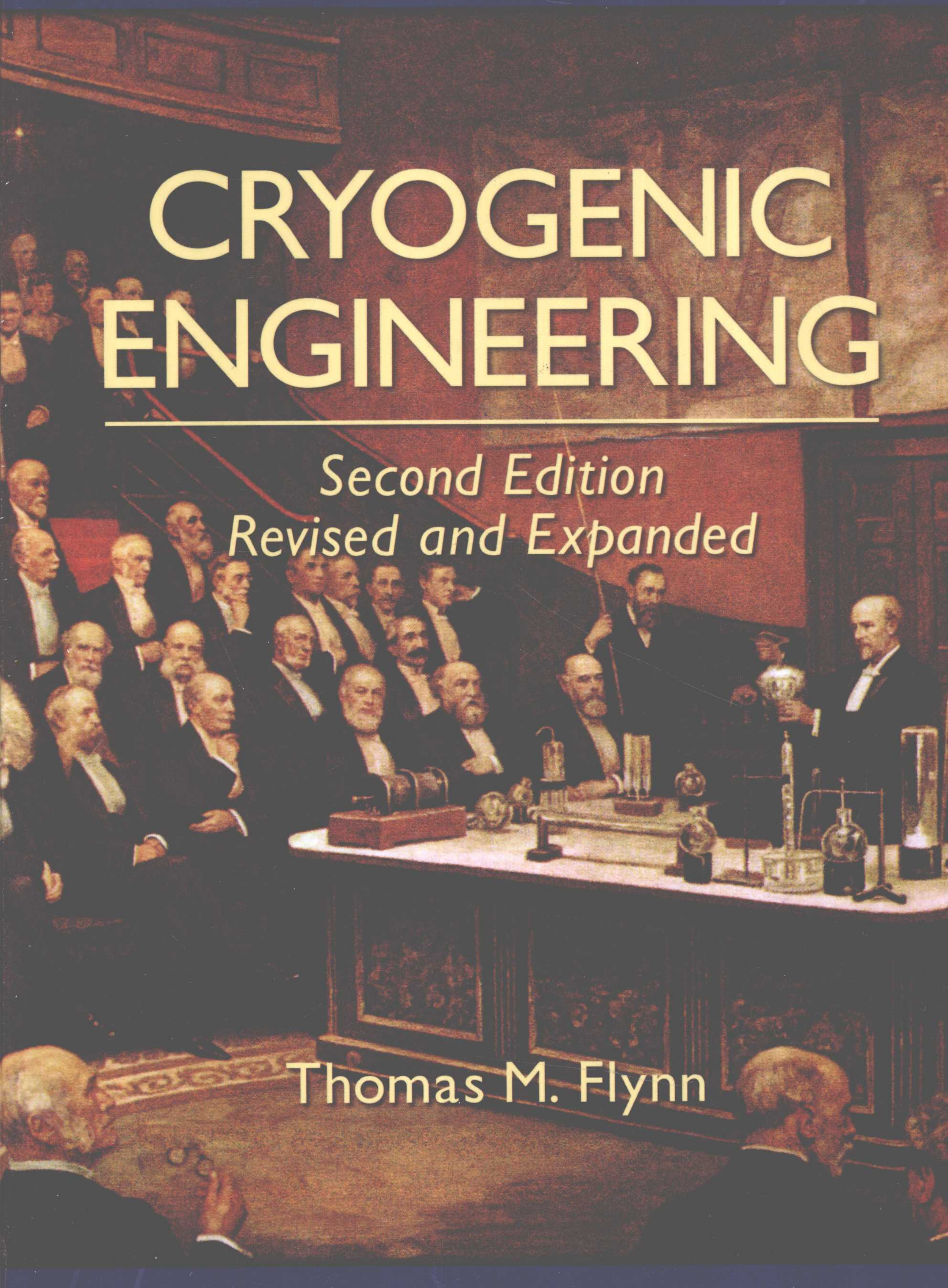
CRYOGENIC ENGINEERING

Second Edition
Revised and Expanded

Thomas M. Flynn



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Preface to the Second Edtion

Dr. Flynn's *Cryogenic Engineering 2nd Edition* was written for a specific audience, namely, the professional engineer or physicist who needs to know some cryogenics to get his or her job done, but not necessarily make a career of it. The 2nd Edition was written to follow closely the cryogenic engineering professional course given annually by Dr. Flynn for 25 years, and accordingly has been thoroughly tested to be very practical. This 2nd (and last) edition includes over 125 new literature citations, and features more than 130 new graphs and tables of data, which may no longer be available elsewhere.

Preface to the First Edition

This book is for the engineer and scientist who work for a living and who need cryogenics to get a job done. It is a deskbook, containing hundreds of tables and chart of cryogenic data that are very hard to come by. Examples and sample calculations of how to use the data are included. It is not a textbook. Instead, it assumes that the reader already has basic engineering and science skills. It is practical, using the measurement units of trade—SI, U.S. customary, and hybrid systems—just as they are commonly used in practice. It is not a design text, but it does contain many useful design guidelines for selecting the right system, either through procurement or in-house construction. In short, it is the cryogenics book I would like to have on my desk.

This book was written to gather into one source much of the technology developed at the National Bureau of Standards (NBS) Cryogenic Engineering Laboratory in Boulder, COL, over the last 40 years.

In the early 1950s, there was a need for the rapid development of a liquid hydrogen technology, and the major responsibility for the progress of this new engineering specialty was entrusted to the Cryogenics Section of the Heat and Power Division of NBS in Washington, D.C. Russell Scott led the work as chief of that section. Scott soon became the individual immediately in charge of the design and construction in Boulder (in March 1952) of the first large-scale liquefier for hydrogen ever built. This was the beginning of the Cryogenic Engineering Laboratory of NBS.

Again, in the late 1950s—when the nation was striving to regain world leadership in the exploration of space—the NBS Cryogenics Engineering Laboratory, which had by then matured under Scott's leadership, assumed a pre-eminent role in the solution of problems important to the nation. Scott, having had the foresight to establish a Cryogenic Data Center within the laboratory, was able to provide a focal point for information on many aspects of cryogenic engineering.

As a result of all this pioneering in the field of low-temperature engineering, a considerable amount of valuable technology was developed that in the course of normal events might have been lost. Scott recognized this, and the result was his book *Cryogenic Engineering*, an important first in its field. Its quality, authority, and completeness constitute a lasting tribute to him.

This present book is a mere shadow of Scott's work but is intended once more to up-date and preserve some of the cryogenics developed at NBS. There is only one author's name on the cover. Nonetheless, this book is a product of the collaboration of hundreds of good men and women of the NBS Cryogenic Engineering Laboratory. It is written to preserve the technology they developed.

When I was about to graduate as a chemical engineer from Rice University in 1955, I proudly told my department chairman, Dr. Arthur J. ("Pappy") Hartsook, that I intended to go to graduate school. Pappy, who knew I was a mediocre student, brightened considerably when I told him I wasn't going to a "good" school, like MIT, Michigan, or Wisconsin. Instead, I was going to the University of Colorado, where I could learn to ski. Dr. Hartsook was so relieved that he gave me a piece of advice pivotal to my career and my life. I will share it with you now. Pappy said that *What* I would work *on* was not nearly as important as *who* I would work *for*.

I took that advice and chose to work for a new professor at the University of Colorado, Dr. Klaus Timmerhaus. Klaus had only been there a year or two; the National Science Foundation and grantsmanship had yet to be invented. I had a teaching assistantship (paper grader) at $150 per month, before taxes. It was the most money I had ever had. To help me get some money for our planned research, Klaus suggested that I work at the Cryogenic Engineering Laboratory of the National Bureau of Standards. And so I did, for the next 28 years. For many years, it was the best of times, a truly nurturing environment for the young engineer scientist, because of the people who either worked there or visited there.

I wish to thank Klaus Timmerhaus, Russell Scott, Bascom Birmingham, Dudley Chelton, Bob Powell, John Dean, Ray Smith, Jo Mandenhall, Jim Draper, Dick Bjorklund, Bill Bulla, M. D. Bunch, Bob Goodwin, Lloyd Weber, Ray Radebaugh, Peter Storch, Larry Sparks, Bob McCarty, Vic Johnson, Bill Little, Bob Paugh, Bob Jacobs, Mike McClintock, Al Schmidt, Pete Vander Arend, Dan Weitzel, Wally Ziegler, John Gardner, Bob Mohling, Bob Neff, Scott Willen, Will Gully, Art Kidnay, Graham Walker, Ralph Surloch, Albert Schuler, Sam Collins, Bill Gifford, Peter Gifford, Ralph Longsworth, Ed Hammel, and Fred Edeskuty. Special thanks are due to Chris Davis and Janet Diaz for manuscript preparation and technical editing. I mention all these names not so much to give credit as to spread the blame.

I apologize in advance to those I have forgotten to mention.

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Cryogenic Engineering Connections

1. FOREWARNED

In his masterpiece, *Civilization*, Sir Kenneth Clark writes not a foreword but rather a fore-warned. Clark writes to the effect that he does not know if his recounting is the actual history of civilization or not. He only knows that his story is his own view of the history of civilization. Having said that, Clark found much relief from the tedium of accuracy and was able to tell a more entertaining, and still highly accurate, story.

I wish to do the same. I do not know if the recounting to follow in this chapter is accurate or not. I only know that it is my own view of how it happened. I hope it is accurate—I did not deliberately make any of it up—but who knows?

I am an American and unabashedly proud of that fact. Therefore, let me begin with the American who may have gotten it all going, John Gorrie (1803–1855).

2. THE ENTREPRENEURS

John Gorrie was born in Charleston South Carolina in 1803 and graduated from the College of Physicians and Surgeons in New York City in 1833. In the spring of 1833 Gorrie moved to Apalachicola, a small coastal town in Florida situated on the Gulf of Mexico at the mouth of the river after which the town is named. By the time he arrived it was already a thriving cotton port, where ships from the north-east arrived to unload cargoes of supplies and load up with cotton for the northern factories. Within a year Gorrie was involved with town affairs. He served as mayor, city treasurer, council member, bank director, and founder of Trinity Church.

In 1834, he was made postmaster and in 1836 president of the local branch of the Pensacola Bank. In the same year, the Apalachicola Company asked him to report on the effects of the climate on the population, with a view to possible expansion of the town. Gorrie recommended drainage of the marshy, low-lying areas that surrounded the town on the grounds that these places gave off a miasma compounded by heat, damp and rotting vegetation which, according to the Spallanzani theory with which every doctor was intimate, carried disease. He suggested that only brick buildings be erected. In 1837, the area enjoyed a cotton boom, and the town population rose to 1500. Cotton bales lined the streets, and in four months 148 ships arrived to unload bricks from Baltimore, granite from Massachusetts, house framing from New York. Gorrie saw that the town was likely to grow as commerce increased and suggested that there was a need for a hospital. There was already a small medical unit in operation under the auspices of the US Government, and Gorrie was employed there on a part-time basis. Most of his patients were sailors and waterside workers, and most of them had fever, which was endemic in Apalachicola every summer.

Gorrie became obsessed with finding a cure to the disease. As early as 1836, he came close to the answer, over 60 years ahead of the rest of the world. In that year he wrote: "Gauze curtains, though chiefly used to prevent annoyance and suffering from mosquitoes, are thought also to be sifters of the atmosphere and interceptors and decomposers of malaria." The suggestion that the mosquito was the disease carrier was not to be made until 1881, many years after Gorrie's death, and for the moment he presumed that it came in some form of volatile oil, rising from the swamps and marshes.

By 1838, Gorrie had noticed that malaria seemed to be connected with hot, humid weather, and he set about finding ways to lower the temperature of his patients in summer. He began by hanging bowls full of ice in the wards and circulating the cool air above them by means of a fan. The trouble was that in Apalachicola ice was hard to come by. Ever since a Massachusetts merchant named Frederic Tudor had hit on the idea of cutting ice from ponds and rivers in winter and storing it in thick-walled warehouses for export to hot countries, regular ice shipments had left the port of Boston for destinations as far away as Calcutta. But Apalachicola was only a small port which the ships often missed altogether: if the ice crop was poor, the price rose to the exorbitant rate of $1.25 a pound. In 1844, Gorrie found the answer to the problem. It was well known that compressed gases which are rapidly allowed to expand absorb heat from their surroundings, so Gorrie constructed a steam engine to drive a piston back and forward in a cylinder. His machine compressed air, causing it to heat, and then the air through radiant coils where it decompressed and cooled, absorbing heat from a bath of brine. On the next cycle the air remained cool, since the brine had given up most of its heat. This air was then pumped out of the cylinder and allowed to circulate in the ward. Gorrie had invented air-conditioning. By bringing the cold brine into contact with water, Gorrie was then able to draw heat from the water to a point where it froze. Gorrie's application of compressed and decompressed gas as a coolant in radiant coils remains the common method for cooling air in modern refrigeration systems. His first public announcement of this development was made on 14 July 1850 in the Mansion House Hotel, where M. Rosan, the French Consul in Apalachicola, was celebrating Bastille Day with champagne. No ice ship had arrived, so the champagne was to be served warm. At the moment of the toast to the French Republic four servants entered, each carrying a silver tray on which was a block of ice the size of a house-brick, to chill the wine, as one guest put it, "by American genius".

In May of the following year Gorrie obtained a patent for the first ice-making machine (see Fig. 1.1), the first patent ever issued for a refrigeration machine. The patent specified that the water container should be placed in the cylinder, for faster freezing. Gorrie was convinced his idea would be a success. The *New York Times* thought differently: "There is a crank," it said, "down in Apalachicola, Florida, who claims that he can make ice as good as God Almighty!" In spite of this, Gorrie advertised his invention as "the first commercial machine to work for ice making and refrigeration." He must have aroused some interest, for later he was in New Orleans, selling the idea that "a ton of ice can be made on any part of the Earth for less than

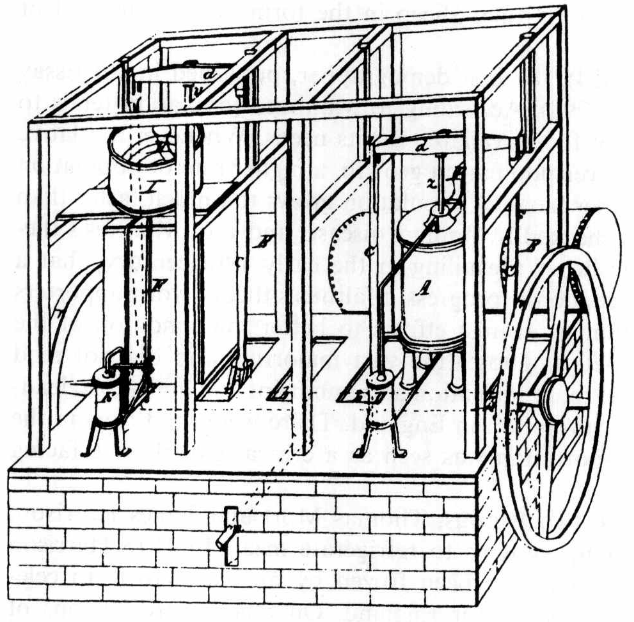

Figure 1.1 Improved process for the artificial production of ice.

$2.00." But he was unable to find adequate backing, and in 1855 he died, a broken and dispirited man. A statue of John Corrie now stands in Statuary Hall of the US Capitol building, a tribute from the State of Florida to his genius and his importance to the welfare of mankind.

Three years after his death a Frenchman, Ferdinand Carré, produced a compression ice-making system and claimed it for his own, to the world's acclaim. Carré was a close friend of M. Rosan, whose champagne had been chilled by Gorrie's machine eight years before.

Just before he died, Gorrie wrote an article in which he said: "The system is equally applicable to ships as well as buildings ... and might be instrumental in preserving organic matter an indefinite period of time." The words were prophetic, because 12 years later Dr. Henry P. Howard, a native of San Antonio, used the air-chilling system aboard the steamship *Agnes* to transport a consignment of frozen beef from Indianola, Texas, along the Gulf of Mexico to the very city where Gorrie had tried and failed to get financial backing for his idea. On the morning of Saturday 10 June 1869, the *Agnes* arrived in New Orleans with her frozen cargo. There it was served in hospitals and at celebratory banquets in hotels and restaurants. The New Orleans *Times Picayune* wrote: "[The apparatus] virtually annihilates space and laughs at the lapse of time; for the Boston merchant may have a fresh juicy beefsteak from the rich pastures of Texas for dinner, and for dessert feast on the delicate, luscious but perishable fruits of the Indies."

At the same time that Howard was putting his cooling equipment into the *Agnes*, committees in England were advising the government that mass starvation was likely in Britain because for the first time the country could no longer feed itself. Between 1860 and 1870, consumption of food increased by a staggering 25%. As the population went on rising, desperate speeches were made about the end of democracy and nationwide anarchy if the Australians did not begin immediately to find a way of sending their sheep in the form of meat instead of tallow and wool.

Thomas Malthus (1766–1834), the first demographer, published in An Essay on the Principle of Population (1798). According to Malthus, population tends to increase faster than the supply of food available for its needs. Whenever a relative gain occurs in food production over population growth, a higher rate of population increase is stimulated; on the other hand, if population grows too much faster than food production, the growth is checked by famine, disease, and war. Malthus's theory contradicted the optimistic belief prevailing in the early 19th century, that a society's fertility would lead to economic progress. Malthus's theory won supporters and was often used as an argument against efforts to better the condition of the poor. (the poor should die quietly). Those (the vast majority) who did not read the complete essay, assumed that mass starvation and imminent and inevitable, leading to the so-called Malthusian revolution in England. There were food riots in the streets. Food storage and transportation was seen as a critical global issue facing mankind.

Partially for these reasons, two Britons, Thomas Mort and James Harrison, emigrated to Australia and set up systems to refrigerate meat. In 1873 Harrison gave a public banquet of meat that had been frozen by his ice factory, to celebrate the departure of the S.S. *Norfolk* for England. On board were 20 tons of mutton and beef kept cold by a mixture of ice and salt. On the way, the system developed a leak and the cargo was ruined. Harrison left the freezing business. Mort then tried a different system, using ammonia as the coolant. He too gave a frozen meat lunch, in 1875, to mark the departure for England of the S.S. *Northam*. Another leak ruined this second cargo, and Mort retired from the business. But both men had left behind them working refrigeration plants in Australia. The only problem was to find the right system to survive the long voyage to London. Eventually, the shippers went back to Gorrie's "dry air" system. Aboard ship, it was much easier to replace leaking air than it was to replace leaking ammonia. Even though ammonia was "more efficient", it was sadly lacking while air was ubiquitous. This NH_3/air substitution is one early example of a lack of "systems engineering". There are often unintended consequences of technology, and the working together of the system as a whole must be considered. NH_3 refrigerators were thermodynamically more efficient, but could not be relished with NH_3 readily.

3. THE BUTCHERS

The development of the air-cycle refrigerator, patented by the Scottish butchers Bell and Coleman in 1877, made the technical breakthrough. The use of atmospheric air as a refrigerating fluid provided a simple, though inefficient, answer to ship-board refrigeration and led to the British domination of the frozen meat trade thereafter.

The first meat cargo to be chilled in this fashion left Australia aboard the S.S. *Strathleven* on 6 December 1879 to dock in London on 2 February of the following year with her cargo intact (Fig. 1.2). Figure 1.3 shows a similar ship to the S.S. Strathleven being unloaded. The meat sold at Smithfield market for between 5*d* and 6*d* per pound and was an instant success. Queen Victoria, presented with a leg of lamb from the same consignment, pronounced it excellent. England was saved.

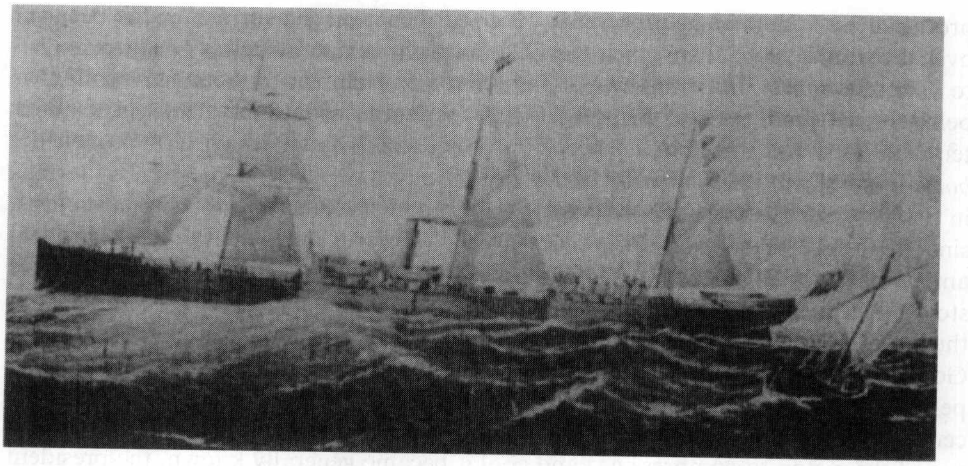

Figure 1.2 The S. S. *Strathleven*, carrying the first successful consignment of chilled beef from Australia to England. Note the cautious mixture of steam and sail, which was to continue into the 20th century.

4. THE BREWERS

Harrison's first attempts at refrigeration in Australia had been in a brewery, where he had been trying to chill beer, and although this operation was a moderate success, the profits to be made from cool beer were overshadowed by the immense potential of the frozen meat market. The new refrigeration techniques were to become a boon to German brewers, but in Britain, where people drank their beer almost at room temperature, there was no interest in chilling it. The reason British beer-drinkers take their beer "warm" goes back to the methods used to make the beer. In Britain it is

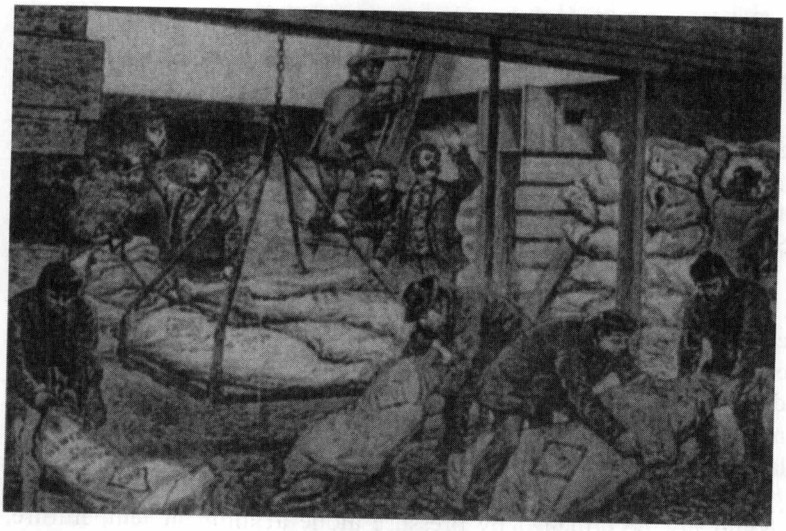

Figure 1.3 Unloading frozen meat from Sydney, Australia, at the South West India Dock, London. This shows the hold of the *Catania*, which left port in August 1881 with 120 tons of meat from the same exporters who had filled the *Strathleven*.

produced by a method using a yeast which ferments on the surface of the beer vat over a period of 5–7 days, when the ideal ambient temperature range is from 60°F to 70°F. Beer brewed in this way suffers less from temperature changes while it is being stored, and besides, Britain rarely experiences wide fluctuations in summer temperatures. But in Germany beer is produced by a yeast which ferments on the *bottom* of the vat. This type of fermentation may have been introduced by monks in Bavaria as early as 1420 and initially was an activity limited to the winter months, since bottom fermentation takes place over a period of up to 12 weeks, in an ideal ambient temperature of just above freezing point. During this time the beer was stored in cold cellars, and from this practice came the name of the beer: lager, from the German verb *lagern* (to store). From the beginning there had been legislation in Germany to prevent the brewing of beer in the summer months, since the higher temperatures were likely to cause the production of bad beer. By the middle of the 19th century every medium-sized Bavarian brewery was using steam power, and when the use of the piston to compress gas and cool it became generally known, the president of the German Brewer's Union, Gabriel Sedlmayr of the Munich Spätenbrau brewery, asked a friend of his called Carl Von Linde if he could develop a refrigerating system to keep the beer cool enough to permit brewing all the year round. Von Linde solved Sedlmayr's problem and gave the world affordable mechanical refrigeration, an invention that today is found in almost every kitchen.

Von Linde used ammonia instead of air as his coolant, because ammonia liquefied under pressure, and when the pressure was released it returned to gaseous form, and in so doing drew heat from its surroundings. In order to compress and release the ammonia, he used Gorrie's system of a piston in a cylinder. Von Linde did not invent the ammonia refrigeration system, but he was the first to make it work. In 1879 he set up laboratories in Wiesbaden to continue research and to convert his industrial refrigeration unit into one for the domestic market. By 1891, he had put 12,000 domestic refrigerators into German and American homes. The modern fridge uses essentially the same system as the one with which Von Linde chilled the Spätenbrau cellars.

5. THE INDUSTRIALISTS

Interest in refrigeration spread to other industries. The use of limelight, for instance, demanded large amounts of oxygen, which could be more easily handled and transported in liquid form. The new Bessemer steel-making process used oxygen. It may be no coincidence that an ironmaster was involved in the first successful attempt to liquefy the gas. His name was Louis Paul Cailletet, and together with a Swiss engineer, Raoul Pictet, he produced a small amount of liquid oxygen in 1877.

At the meeting of the Académie des Sciences in Paris on 24 December 1887, two announcements were made which may be recognized as the origins of cryogenics as we know it today. The secretary to the Académie spoke of two communications he had received from M. Cailletet working in Paris and from Professor Pictet in Geneva in which both claimed the liquefaction of oxygen, one of the permanent gases.

The term "permanent" had arisen from the experimentally determined fact that such gases could not be liquefied by pressure alone at ambient temperature, in contrast to the nonpermanent or condensable gases like chlorine, nitrous oxide and carbon dioxide, which could be liquefied at quite modest pressures of 30–50 atm. During the previous 50 years or so, in extremely dangerous experiments, a number of workers had discovered by visual observation in thick-walled glass tubes that the permanent gases, including hydrogen, nitrogen, oxygen and carbon monoxide, could not be liquefied at pressures as high as 400 atm. The success of these experimenters marked the end of the idea of permanent gases and established the possibility of liquefying any gas by moderate compression at temperatures below the critical temperature. In 1866, Van der Waals (1837–1923), had published his first paper on "the continuity of liquid and gaseous states" from which the physical understanding of the critical state, and of liquefaction and evaporation, was to grow.

Cailletet had used the apparatus shown in Fig. 1.4 to produce a momentary fog of oxygen droplets in the thick-walled glass tube. The oxygen gas was compressed using the crude Natterer compressor in which pressures up to 200 atmospheres were generated by a hand-operated screw jack. The pressure was transmitted to the oxygen gas in the glass tube by hydraulic transmission using water and mercury. The gas was cooled to −103°C by enclosing the glass tube with liquid ethylene and was then expanded suddenly by releasing the pressure via the hand wheel. A momentary fog was seen, and the procedure could then be repeated for other observers to see the phenomenon.

Figure 1.5 shows the cascade refrigeration system used by Professor Pictet at the University of Geneva in which oxygen was first cooled by sulphur dioxide and then by liquid carbon dioxide in heat exchangers, before being expanded into the atmosphere by opening a valve. The isenthalpic expansion yielded a transitory jet of partially liquefied oxygen, but no liquid could be collected from the high-velocity jet. The figure shows how Pictet used pairs of compressors to drive the SO_2 and CO_2 refrigerant cycles. This is probably one of the first examples of the cascade refrigeration system invented by Tellier (1866) operating at more than one temperature level. Pictet was a physicist with a mechanical flair, and although he did not

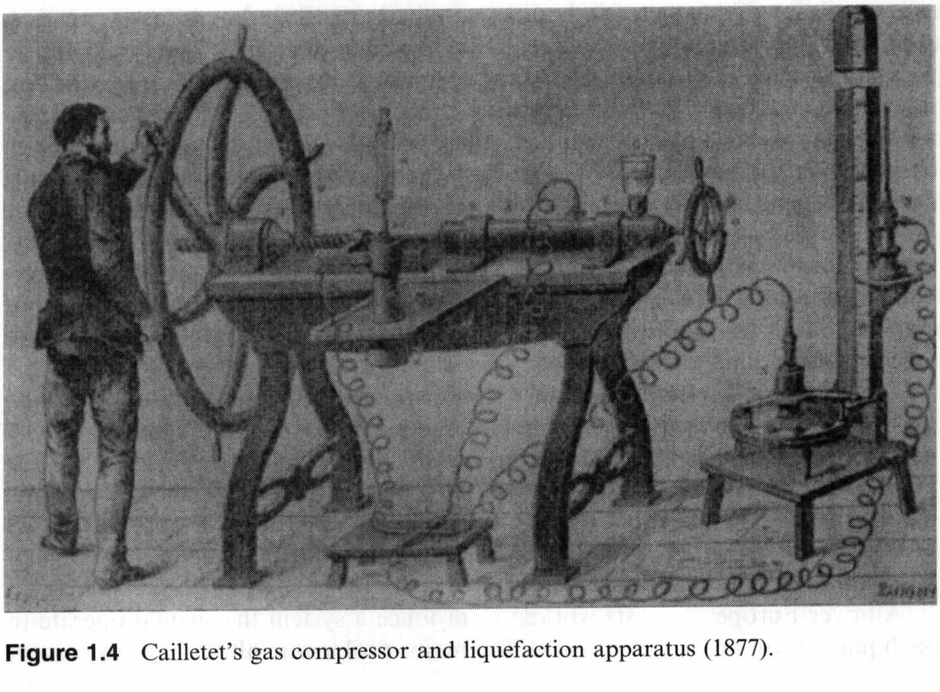

Figure 1.4 Cailletet's gas compressor and liquefaction apparatus (1877).

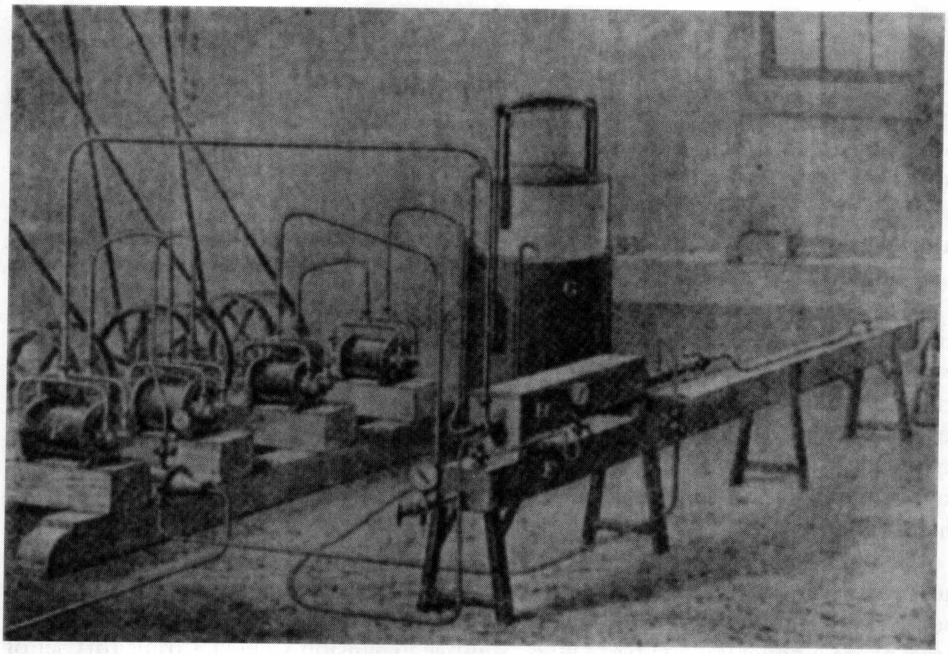

Figure 1.5 Pictet's cascade refrigeration and liquefaction system (1877).

pursue the liquefaction of oxygen (he made a name developing ice-skating rinks), his use of the cascade system inspired others like Kamerlingh Onnes and Dewar.

In the early 1880s one of the first low-temperature physics laboratories, the Cracow University Laboratory in Poland, was established by Szygmunt von Wroblewski and K. Olszewski. They obtained liquid oxygen "boiling quietly in a test tube" in sufficient quantity to study properties in April 1883. A few days later, they also liquefied nitrogen. Having succeeded in obtaining oxygen and nitrogen as true liquids (not just a fog of liquid droplets), Wroblewski and Olszewski, now working separately at Cracow, attempted to liquefy hydrogen by Cailletet's expansion technique. By first cooling hydrogen in a capillary tube to liquid-oxygen temperatures and expanding suddenly from 100 to 1 atm, Wroblewski obtained a fog of liquid-hydrogen droplets in 1884, but he was not able to obtain hydrogen in the completely liquid form.

The Polish scientists at the Cracow University Laboratory were primarily interested in determining the physical properties of liquefied gases. The ever-present problem of heat transfer from ambient plagued these early investigators because the cryogenic fluids could be retained only for a short time before the liquids boiled away. To improve this situation, an ingenious experimental technique was developed at Cracow. The experimental test tube containing a cryogenic fluid was surrounded by a series of concentric tubes, closed at one end. The cold vapor arising from the liquid flowed through the annular spaces between the tubes and intercepted some of the heat traveling toward the cold test tube. This concept of *vapor shielding* is used today in conjunction with high-performance insulations for the long-term storage of liquid helium in bulk quantities.

All over Europe scientists worked to produce a system that would operate to make liquid gas on an industrial scale. The major problem in all this was to prevent