# CRYOGENIC ENGINEERING

Second Edition Revised and Expanded

## Thomas M. Flynn

## CRYOGENIC ENGINEERING

Second Edition Revised and Expanded

## CRYOGENIC ENGINEERING

## Second Edition Revised and Expanded

## Thomas M. Flynn

CRYOCO, Inc. Louisville, Colorado, U.S.A.



New York

CRC Press Taylor & Francis Group 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, FL 33487-2742

© 2004 by Taylor & Francis Group, LLC CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works Version Date: 20130723

International Standard Book Number-13: 978-0-203-02699-1 (eBook - PDF)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (http:// www.copyright.com/) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

**Trademark Notice:** Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at http://www.taylorandfrancis.com

and the CRC Press Web site at http://www.crcpress.com

The places I took him! I tried hard to tell Young Conrad Cornelius o'Donald o'Dell A few brand new wonderful words he might spell. I led him around and I tried hard to show There are things beyond Z that most people don't know. I took him past Zebra. As far as I could. And I think, perhaps, maybe I did him some good...

On Beyond Zebra, by Dr. Seuss. With permission, Random House Inc. 1745 Broadway, New York, NY.

To Rita

### Preface to the Second Editon

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.

### Contents

Preface to the Second Edition v Preface to the First Edition vii
<ul> <li>1. Cryogenic Engineering Connections</li></ul>
2. Basic Principles       23         1. Introduction       23         2. Thermodynamics       27         3. Heat Transfer       55         4. Momentum Transfer       68         5. Heat Leak and Pressure Drop in Cryogenic Transfer Lines       69         6. Cooldown       73         7. Summary       76
<ul> <li>3. Cryogenic Fluids</li></ul>
<ul> <li>4. Mechanical Properties of Solids</li></ul>

5. Low-Temperature Strength of Solids . . . . 268 6. Elastic Constants . . . 274 7. Modulus of Elasticity . . . 279 8. Fatigue Strength . . . 282 9. Mechanical Properties Summary . . . . 284 10. Design Considerations . . . . 285 11. Material Selection Criteria for Cryogenic Tanks . . . . 291 1. Thermal Properties . . . 301 2. Emissivity, Absorptivity, and Reflectivity . . . . 327 3. Electrical Properties . . . . 332 4. Superconductivity . . . . 339 1. Introduction . . . . 359 2. Refrigeration and Liquefaction . . . . 359 3. Recuperative Cycles . . . . 367 4. Liquefaction of Gases . . . . 369 5. Refrigerator Efficiency . . . . 377 6. Useful Thermodynamic Relations . . . . 380 7. Refrigeration and Liquefaction Methods . . . . 381 8. Large Systems . . . . 401 9. Regenerative Cycles . . . . 401 10. Magnetocaloric Refrigeration . . . . 427 11. Ultra Low-Temperature Refrigerators . . . . 433 12. Very Small Coolers . . . . 438 13. Superconductors and Their Cooling Requirements . . . . 439 14. Cryocoolers . . . . 441 15. Conclusion . . . . 442 7. Insulation 1. Introduction . . . . 445 2. Heat Transfer . . . . 446 3. Vacuum Insulation . . . . 448 4. Evacuated Porous Insulation . . . . 468 5. Gas-Filled Powders and Fibrous Materials . . . . 475 6. Solid Foams . . . . 477 7. Multilayer Insulation . . . 483 8. Vapor Barriers . . . . 510 9. Protective Enclosures . . . . 513 10. Liquid and Vapor Shields . . . . 514 11. Composite Insulations . . . . 518 12. Other Materials . . . . 525 13. Placement of Insulation Systems . . . . 525 14. Adhesives . . . . 526

#### Preface

<ul><li>15. Comparison of Insulations 528</li><li>16. Summary 535</li></ul>	
<ul> <li>8. Cryogenic Instrumentation</li></ul>	537
<ul> <li>9. Cryogenic Equipment and Cryogenic Systems Analysis</li> <li>1. Introduction 633</li> <li>2. Compressors 638</li> <li>3. Pumps 644</li> <li>4. Expansion Engines 652</li> <li>5. Valves 665</li> <li>6. Heat Exchangers 671</li> <li>7. Storage 696</li> <li>8. Transfer of Liquefied Gases 714</li> </ul>	633
<ol> <li>Natural Gas Processing and Liquefied Natural Gas</li> <li>Introduction 727</li> <li>Purification 730</li> <li>Hydrocarbon Recovery 742</li> <li>Cryogenic Upgrading of Natural Gas 745</li> <li>Helium Extraction, Nitrogen Rejection, and Hydrocarbon Recovery 748</li> <li>Liquefaction of Natural Gas 748</li> </ol>	727
<ul> <li>11. Safety with Cryogenic Systems</li> <li>1. Introduction 773</li> <li>2. Physiological Hazards 773</li> <li>3. Suitability of Materials and Construction Techniques 777</li> <li>4. Explosions and Flammability 788</li> <li>5. Excessive Pressure Gas 806</li> <li>6. Special Considerations for Hydrogen 811</li> <li>7. Special Considerations for Oxygen 837</li> <li>8. General Safety Principles 865</li> <li>9. Safety Checklist 869</li> </ul>	773
References	873
Index	891

#### 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<sub>3</sub>/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<sub>3</sub> refrigerators were thermodynamically more efficient, but could not be relished with NH<sub>3</sub> 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 5d and 6d 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  $60^{\circ}$ 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  $-103^{\circ}$ 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<sub>2</sub> and CO<sub>2</sub> 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

the material from drawing heat from its surroundings. In 1882, a French physicist called Jules Violle wrote to the French Academy to say that he had worked out a way of isolating the liquid gas from its surroundings through the use of a vacuum. It had been known for some time that vacua would not transmit heat, and Violle's arrangement was to use a double-walled glass vessel with a vacuum in the space between the walls. Violle has been forgotten, his place taken by a Scotsman who was to do the same thing, much more efficiently, eight years later. His name was Sir James Dewar, and he added to the vessel by silvering it both inside and out (Violle had only silvered the exterior), in order to prevent radiation of heat either into or out of the vessel.

#### 6. THE SCIENTISTS

James Dewar was appointed to the Jacksonian Professorship of Natural Philosophy at Cambridge in 1875 and to the Fullerian Professorship of Chemistry at The Royal Institution in 1877, the two appointments being held by him until his death at the age of 81 in 1923. Dewar's research interests ranged widely but his outstanding work was in the field of low temperatures. Within a year of his taking office at The Royal Institution, the successful liquefaction of oxygen by Cailletet and Pictet led Dewar to repeat Cailletet's experiment. He obtained a Cailletet apparatus from Paris, and, within a few months, in the summer of 1878 he demonstrated the formation of a mist of liquid oxygen to an audience at one of his Friday evening discourses at The Royal Institution. This lecture was the first of a long series of demonstrations, extending over more than 30 years and culminating in dramatic and sometimes hazardous demonstrations with liquid hydrogen (Fig. 1.6). In May 1898 Dewar produced 20 cm<sup>3</sup> of liquid hydrogen boiling quietly in a vacuum-insulated tube, instead of a mist.

The use of a vacuum had been used by Dewar and others as early as 1873 and his experiments over several years before 1897 went on to show how he could obtain significant reductions (up to six times) by introducing into the vacuum space powders such as charcoal, lamp black, silica, alumina, and bismuth oxide. For this purpose, he used sets of three double-walled vessels connected to a common vacuum in which one of the set was used as a control. Measurement of the evaporation rate of liquid air in the three vessels then enabled him to make comparative assessments on the test insulations.

In 1910 Smoluchowski demonstrated the significant improvement in insulating quality that could be achieved by using evacuated powders in comparison with unevacuated insulations. In 1937, evacuated-powder insulations were first used in the United States in bulk storage of cryogenic liquids. Two years later, the first vacuum-powder-insulated railway tank car was built for the transport of liquid oxygen.

Following evacuated powders, he made further experiments using metallic and other septa-papers coated with metal powders in imitation of gold and silver, together with lead and aluminum foil and silvering of the inner surfaces of the annular space. He found that three turns of aluminum sheet (not touching) were not as good as silvered surfaces. Had he gone on to apply further turns of aluminum, he would have discovered the principle of multilayer insulation which we now know to be superior to silvering. Nevertheless, his discovery of silvering as an effective means of reducing the radiative heat flux component was a breakthrough. From 1898, the glass Dewar flask quickly became the standard container for cryogenic



**Figure 1.6** Sir James Dewar lecturing at the Royal Institution. Although Violle preceded Dewar in the development of the vacuum flask, there is no evidence that Dewar knew of his work when he presented the details of his new container to the Royal Institution in 1890.

liquids. Meanwhile his work on the absorptive capacity of charcoal at low temperatures paved the way towards the development of all-metal, double-walled vacuum vessels.

Another first for Dewar was his use of mixtures of gases to enhance J-T cooling, a topic revisited in cryogenics in 1995.

Historically, the expansion of a mixture of hydrogen and nitrogen was employed by Dewar in 1894 in attempts to liquefy hydrogen at that time. Dewar wrote: "Expansion into air at one atmosphere pressure of a mixture of 10% nitrogen in hydrogen yielded a much lower temperature than anything that has been recorded up to the present time."

Because his flasks (unlike those of Jules Violle) were silvered inside and out, Dewar's flasks could equally well retain heat as cold. Dewar's vessel became known in scientific circles as the Dewar flask; with it, he was able to use already liquid gases

to enhance the chill during the liquefaction of gases whose liquefaction temperature was lower than that of the surrounding liquid. In this way, in 1891, he succeeded for the first time in liquefying hydrogen.

Dewar had considerable difficulty in finding competent glass makers willing to undertake the construction of his double-walled vessels and had been forced to get them made in Germany.

By 1902 a German called Reinhold Burger, whom Dewar had met when visiting Germany to get his vessels made, was marketing them under the name of Thermos. The manufacture of such vessels developed into an important industry in Germany as the Thermos flask, and this monopoly was maintained up to 1914. Dewar never patented his silvered vacuum flask and therefore never benefited financially from his invention.

The word "Cryogenics" was slow in coming.

The word cryogenics is a product of the 20th Century and comes from the Greek— $\kappa\rho o\varsigma$ —frost and— $\gamma i\nu o\mu \alpha i$ —to produce, engender. Etymologically, cryogenics means the science and art of producing cold and this was how Kamerlingh Onnes first used the word in 1894. Looking through the papers and publications of Dewar and Claude, it appears that neither of them ever used the word; indeed a summary of Dewar's achievements by Armstrong in 1916 contains no mention but introduces yet another term, "the abasement of temperature."

In 1882, Kamerlingh Onnes (1853–1926) was appointed to the Chair of Experimental Physics at the University of Leiden in the Netherlands and embarked on building up a low-temperature physics laboratory in the Physics Department. The inspiration for his laboratory was provided by the systematic work of Van der Waals at Amsterdam, and subsequently at Leiden, on the properties of gases and liquids. In 1866, Van der Waals 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.

He operated an open-door policy encouraging visitors from many countries to visit, learn, and discuss. He published all the experimental results of his laboratory, and full details of the experimental apparatus and techniques developed, by introducing in 1885 a new journal "Communications from the Physical Laboratory at the University of Leiden."

As a result, he developed a wide range of contacts and a growing track record of success, so that from the turn of the century his Leiden laboratory held a leading position in cryogenics for almost 50 years, certainly until the mid-1930s. In 1908, for example, he won the race with Dewar and others to liquefy helium and went on to discover superconductivity in 1911.

Onnes' first liquefaction of helium in 1908 was a tribute both to his experimental skill and to his careful planning. He had only 360 L of gaseous helium obtained by heating monazite sand from India. More than  $60 \text{ cm}^3$  of liquid helium was produced by Onnes in his first attempt. Onnes was able to attain a temperature of 1.04 K in an unsuccessful attempt to solidify helium by lowering the pressure above a container of liquid helium in 1910.

It is interesting to compare Dewar's approach with that of his rival, Kamerlingh Onnes. Having successfully liquefied hydrogen in 1898, Dewar had been able to monopolize the study of the properties of liquid hydrogen and published many papers on this subject. His attempts in 1901 to liquefy helium in a Cailletet tube cooled with liquid hydrogen at 20.5 K, using a single isentropic expansion from pressures up to 100 atm, led at first to a mist, being clearly visible. Dewar was

suspicious of a contamination because after several compressions and expansions, the end of the Cailletet tube contained a small amount of solid that sublimed to a gas without passing through the liquid state when the liquid hydrogen was removed. On lowering the temperature of the liquid hydrogen by pumping to 16 K, and repeating the expansions on the gas from which the solid had been separated by the previous expansions at 20.5 K, no mist was seen. From these observations, he concluded that the mist was caused by some material other than helium, in all probability neon, and that the critical temperature and boiling point of helium were below 9 K and about 5 K, respectively.

The Cailletet tube was, of course, limited in its potential and Dewar appreciated that he needed a continuous circulation cascade system employing liquid hydrogen at reduced pressure and a final stage of Joule–Thomson expansion with recuperative cooling. He already had at the Royal Institution a large quantity of hardware, compressors, and pumps for the cascade liquefaction system he had assembled for liquefying hydrogen. From 1901, he joined the race to liquefy helium with competitors like Travers and Ramsay at University College, London, Kamerlingh Onnes and his Leiden team, and Olszewski at Cracow. The race continued for 7 years until 1908 when the Leiden team won. Dewar and the other competitors perhaps failed because they had not appreciated that the magnitude of the effort to win the race required a systems approach to solve the problems of purification, handling small quantities of precious helium gas, maintaining leaky compressors, improving the design of recuperative heat exchangers, and understanding the properties and behavior of fluids and solids at low temperatures, all at the same time.

As a direct result of their success, the Leiden team of Kamerlingh Onnes went on to discover superconductivity in 1911 and thereafter maintained a leading position in low-temperature research for many years.

#### 7. THE ENGINEERS

Dr. Hampson was medical officer in charge of the Electrical and X-ray Departments, Queens and St. John's Hospitals, Leicester Square, London. He was a product of the Victorian age, with a classics degree at Oxford in 1878, having subsequently acquired his science as an art and a living; but he possessed an extraordinary mechanical flair. He was completely overshadowed by Dewar at The Royal Institution, Ramsay at University College and Linde at Wiesbaden, each with their considerable laboratory facilities. Indeed, Dewar seems to have been unable to accept Hampson as a fellow experimentalist or to acknowledge his contribution to cryogenics.

And yet, Hampson with his limited facilities was able to invent and develop a compact air liquefier which had a mechanical elegance and simplicity which made Dewar's efforts crude and clumsy in comparison. Indeed, Hampson's design of heat exchanger was so successful that it is still acknowledged today. The Hampson type coiled tube heat exchanger is widely used today. In 1895, when Hampson and Linde independently took out patents on their designs of air liquefier, the Joule–Thomson effect was known and the principle of recuperative cooling by so-called self-intensification had been put forward by Siemens as early as 1857. The step forward in both patents was to break away from the cascade system of cooling and to rely entirely on Joule–Thomson cooling together with efficient heat exchanger designs.



Figure 1.7 Linde two-stage compressor and 3 L/hr air liquefier (1895).

Linde used concentric tubes of high-pressure line enclosed by a low-pressure return, the two being wound into a single layer spiral to achieve a compact design (Fig. 1.7). "Compact" is a relative term. Linde's first such heat exchanger was made of hammered copper tubing approximately one-quarter of an inch thick. The outer (low pressure) tube was more than 6 in. in diameter. It is said that it took the better part of a month for the heat exchanger to cool down and achieve thermal equilibrium.

After 1895, Linde made rapid progress in developing his Joule–Thomson expansion liquefier making some 3 L of liquid air per hour.

By the end of 1897, Charles Tripler, an engineer in New York had constructed a similar but much larger air liquefier, driven by a 75 kW steam engine, which produced up to 15 L of liquid air per hour (Fig. 1.8). Tripler discovered a market for liquid air as a medium for driving air expansion engines—the internal combustion engine was still unreliable at that time—and he succeeded in raising \$10 M on Wall Street to launch his Liquid Air Company.

Using the liquid air he had produced to provide high-pressure air for an air expansion engine to drive his air compressor, he was convinced that he could make more liquid air than he consumed—and coined the word "surplusage." He was of course wrong. In 1902, Tripler was declared bankrupt, and Wall Street and the US lost interest in commercial applications of cryogenics for many years to come, although important cryophysics and cryo-engineering research continued in US universities.

In 1902 Georges Claude, a French engineer, developed a practical system for air liquefaction in which a large portion of the cooling effect of the system was obtained through the use of an expansion engine. The use of an expansion engine



Figure 1.8 Tripler's air liquefier with steam-driven compressor and tube-in-shell heat exchangers (1898).

caused the gas to cool isentropically rather than isenthalpically, as is the case in Joule–Thomson expansion. Claude's first engines were reciprocating engines using leather seals (actually, the engines were simply modified steam engines). During the same year, Claude established l'Air Liquide to develop and produce his systems. The increase in cooling effect over the Joule–Thomson expansion of the Linde/Hampson/Tripler designs was so large as to constitute another technical breakthrough. Claude went on to develop air liquefiers with piston expanders in the newly formed Société L'Air Liquide.

Although cryogenic engineering is considered a relatively new field in the US, it must be remembered that the use of liquefied gases in US industry began in the early 1900s. Linde installed the first air-liquefaction plant in the United States in 1907, and the first American-made air-liquefaction plant was completed in 1912. The first commercial argon production was put into operation in 1916 by the Linde company in Cleveland, Ohio. In 1917 three experimental plants were built by the Bureau of Mines, with the cooperation of the Linde Company, Air Reduction Company, and the Jefferies-Norton Corporation, to extract helium from natural gas of Clay County, Texas. The helium was intended for use in airships for World War I. Commercial production of neon began in the United States in 1922, although Claude had produced neon in quantity in France since 1920.

Around 1947 Dr. Samuel C. Collins of the department of mechanical engineering at Massachusetts Institute of Technology developed an efficient liquid-helium laboratory facility. This event marked the beginning of the period in which liquidhelium temperatures became feasible and fairly economical. The Collins helium cryostat, marketed by Arthur D. Little, Inc., was a complete system for the safe, economical liquefaction of helium and could be used also to maintain temperatures at any level between ambient temperature and approximately 2 K.

The first buildings for the National Bureau of Standards Cryogenic Engineering Laboratory were completed in 1952. This laboratory was established to provide engineering data on materials of construction, to produce large quantities of liquid hydrogen for the Atomic Energy Commission, and to develop improved processes and equipment for the fast-growing cryogenic field. Annual conferences in cryogenic engineering have been sponsored by the National Bureau of Standards (sometimes sponsored jointly with various universities) from 1954 (with the exception of 1955) to 1973. At the 1972 conference at Georgia Tech in Atlanta, the Conference Board voted to change to a biennial schedule alternating with the Applied Superconductivity Conference. The NBS Cryogenic Engineering Laboratory is now part of history, as is the name "NBS", now the National Institutes for Science and Technology (NIST).

#### 8. THE ROCKET SCIENTISTS

The impact of cryogenics was wide and varied. The Dewar flask changed the social habits of the Edwardian well-to-do: picnics became fashionable because of it. In time it changed the working-man's lunch break and accompanied expeditions to the tropics and to the poles, carrying sustenance for the explorers and returning with hot or cold specimens. Later, it saved thousands of lives by keeping insulin and other drugs from going bad. Perhaps its most spectacular impact was made, however, by two men whose work went largely ignored, and by a third who did his work in a way that could not be ignored. The first was a Russian called Konstantin Tsiolkovsky, whose early use of liquid gas at the beginning of the 20th century was to lie buried under governmental lack of interest for decades. The second was an American called Robert Goddard, who did most of his experiments on his aunt's farm in Massachusetts, and whose only reward was lukewarm interest from the weather bureau.

On 16 March 1926, Dr. Robert H. Goddard conducted the world's first successful flight of a rocket powered by liquid-oxygen–gasoline propellant on a farm near Auburn, Massachusetts. This first flight lasted only  $2\frac{1}{2}$  sec, and the rocket reached a maximum speed of only 22 m/s (50 mph). Dr. Goddard continued his work during the 1930s, and by 1941 he had brought his cryogenic rockets to a fairly high degree of perfection. In fact, many of the devices used in Dr. Goddard's rocket systems were used later in German V-2 weapons systems (Fig 1.9).

The third was a German, Herman Oberth, and his work was noticed because it aimed at the destruction of London.

His liquid gases were contained in a machine that became known as Vengeance Weapon 2, or V-2, and by the end of the Second World War it had killed or injured thousands of military and civilian personnel. All three men had realized that certain gases burn explosively, in particular hydrogen and oxygen, and that, since in their liquid form they occupy less space than as a gas (hydrogen does this by a factor of 790) they were an ideal fuel. Thanks to the principles of the Dewar flask, they could be stored indefinitely, transported without loss, and contained in a launch vehicle that was essentially a vacuum flask with pumps, navigation systems, a combustion chamber and a warhead.

(One of Oberth's most brilliant assistants was a young man called Werner von Braun, and it was he who brought the use of liquid fuel to its most spectacular expression when his brainchild, the Saturn V, lifted off at Cape Canaveral on 16 July 1969, carrying Armstrong, Aldrin, and Collins to their historic landing on the moon.)



**Figure 1.9** The V-2 liquid-fueled rocket used a mixture of oxygen and kerosene. Originally developed at the experimental rocket base in Peenemunde, on the Baltic, the first V-2 landed in London in 1944. When the war ended, German engineers were working on a V-3 capable of reaching New York.

There is no doubt that the development of today's space technology would have been impossible without cryogenics. The basic reason for this lies with the high specific impulse attainable with kerosene/liquid oxygen (2950 m/s) and liquid hydrogen/liquid oxygen (3840 m/s)—values much higher than with liquid or solid propellants stored at ambient temperatures.

Space cryogenics developed rapidly in the early 1960s for the Apollo rocket series, at the same time as LNG technology. The driving force for space cryogenics development was the competition between the US and Russia in the exploration of Space, and the surface of the Moon in particular, and in the maintenance of detente in the "cold war".

Particular requirements then, and now in the Space Shuttle flight series, include the use of liquid hydrogen as a propellant fuel, liquid oxygen as a propellant oxidizer and for the life support systems, both liquids for the fuel cell electric power supplies and liquid helium to pressurize the propellant tanks. The successful development of the necessary cryogenic technology has provided an extraordinary range of spin-offs and a remarkable level of confidence in the design, construction, and handling of cryogenic systems.

#### 9. THE PHYSICISTS AND SUPERCONDUCTIVITY

The phenomenon of zero electrical resistance was discovered in 1911 in mercury by Kamerlingh Onnes and his team at Leiden. Although he realized the great

significance of his discovery, Kamerlingh Onnes was totally frustrated by the lack of any practical application because he found that quite small magnetic fields, applied either externally or as self-fields from internal electric currents, destroyed the superconducting state. The material suddenly quenched and acquired a finite electrical resistance.

For the next 50 years, very little progress was made in applying superconductivity, although there was a growing realization that a mixed state of alternate laminae of superconducting and normal phase had a higher critical field which depended on the metallurgical history of the sample being studied. In fact, an impasse had arisen by the late 1950s, and little progress was being achieved on the application of superconductivity.

On the other hand, great progress had been achieved by this time in the UK, USSR, and US in the theoretical description of superconductivity. This progress stemmed largely from two sets of experimental evidence; firstly, demonstrations of the isotope effect, indicating that lattice vibrations must play a central role in the interaction leading to superconductivity; secondly, the accumulation of evidence that an energy gap exists in the spectrum of energy states available to the conduction electrons in a superconductor. In 1956, Bardeen, Cooper, and Schrieffer (see Table 1.1. for a list of the many Nobel Laureates indebted to cryogenics) proposed a successful theory of superconductivity in which conduction electrons are correlated in pairs with the same center of mass momentum via interactions with the lattice. The theory made predictions in remarkably good agreement with experimental data and provided the basis for later developments such as quantum mechanical tunneling, magnetic flux quantization, and the concept of coherence length.

The break out of the impasse in the application of superconductivity came from systematic work at the Bell Telephone Laboratories, led by Matthias and Hulm. In 1961, they published their findings on the brittle compound Nb<sub>3</sub>Sn, made by the high-temperature treatment of tin powder contained in a Niobium capillary tube. This compound retained its superconductivity in a field of 80 KG (8 Tesla), the highest field available to them, while carrying a current equivalent to a density of 100,000 A/cm<sup>2</sup>. The critical field at 4.2 K, the boiling point of helium, was much greater than 8 T and was therefore at least 100 times higher than that of any previous superconductor.

This finding was followed by the discovery of a range of compounds and alloys with high critical fields, including NbZr, NbTi, and  $V_3Ga$ ; the race was on to manufacture long lengths of wire or tape and develop superconducting magnets for commercial applications. At first, the early wires were unstable and unreliable and it soon became clear that a major research effort was needed.

#### 9.1. High Field, Type 2 Superconductivity (1961)

In any event, NbTi turned out to be a much easier material to develop than  $Nb_3Sn$ , because it was ductile. However, it took 10 years or more to develop reliable, internally stabilized, multifilamentary composite wires of NbTi and copper. Only then, around 1970, was it possible for high field and large-scale applications of superconductivity to be considered with confidence.

#### 9.2. The Ceramic Superconductors

All previous developments in superconductivity were eclipsed in 1986 by the discovery of a new type of superconductor composed of mixtures of ceramic oxides. By the

1902 Pieter Zeeman	Influence of magnetism upon radiation
1910 Johannes Van der Waals	The equation of state of gases and liquids
1913 H. Kamerlingh Onnes	The properties of materials at low temperature, the preparation of liquid helium
1920 Charles Guillaume	Materials for national prototype standards (Ni-Steel) INVAR
1934 H. C. Urey	Discovery of deuterium produced by the distillation of liquid hydrogen
1936 P.J.W. Debye	The behavior of substances at extremely low temperatures, especially heat capacity
1950 Emmanuel Maxwell	"Isotope Effect" in superconductivity
1956 John Bardeen	Semiconductors and superconductivity
1957 Tsung Dao Lee.	Upsetting the principle of conservation of
Chen Ning Yang	parity as a fundamental law of physics
1960 D. A. Glaser	Invention of bubble chamber
1961 R. L. Mössbauer	Recoil-less nuclear resonance absorption of gamma radiation
1962 L. D. Landau	Pioneering theories of condensed matter especially liquid He <sup>3</sup>
1968 Louis W. Alvarez	Decisive contributions to elementary particle physics, through his development of hydrogen bubble chamber technique and data analysis
1972 John Bardeen, Leon N. Cooper, L. Robert Schrieffer	BCS theory of superconductivity
1973 B. D. Josephson, Ivar Giaever, Leo Esaki	The discovery of tunneling supercurrents (The Josephson Junction)
1978 Peter Kapitza	Methods pf making liquid helium and the characterization of Helium II as a "superfluid".
1987 J. G. Bednorz, K.A. Muller	High-temperature superconductors
1996 D. Lee, D. D. Osheroff, R.C. Richardson	Discovery of superfluidity in liquid helium-3
1997 Steven Chu, Claude Cohen-Tannoudii	Methods to cool and trap atoms with lasers
1998 R. B. Laughlin, H. L. Stormer	Discovery of a new form of quantum fluid
D C Tsui	excitations at low temperatures
2001 Eric Cornell W Ketterle	For achieving the Bose–Einstein condensate
Carl Wieman	at near absolute zero

**Table 1.1** Nobel Laureates Linked with Cryogenics

end of 1987, superconducting critical temperatures of ceramic materials had risen to 90 K for Y–Ba–Cu–O; 110 K for Bi–Sr–Ga–Cu–O; and 123 K for Tl–Ba–Ca–Cu–O. These temperatures are about ten times higher than the critical temperatures of previous metallic superconductors, thereby allowing liquid nitrogen instead of liquid helium to be used as a cooling medium.

This discovery changes the economics and practicability of engineering applications of superconductivity in a dramatic way. Refrigeration costs with liquid nitrogen are 100 times cheaper than those with liquid helium, and only simple one-stage

1848	John Gorrie produces first mechanical refrigeration machine
1857	Siemens suggests recuperative cooling or "self-intensification"
1866	Van der Waals first explored the critical point, essential to the work of Dewar and Onnes
1867	Henry P. Howard of San Antonio Texas uses Gorrie's air-chilling system to transport frozen beef from Indianola TX to cities along the Gulf of Mexico
1869	Malthusian revolution in England, predicting worldwide starvation
1873	James Harrison attempts to ship frozen beef from Australia to the UK aboard the SS <i>Norfolk.</i> , the project failed
1875	Thomas Mort tries again to ship frozen meat from Australia to the UK, this time aboard the SS <i>Northam</i> . Another failure. Gorrie's air system eventually produce success by Bell and Coleman 1877
1877	Coleman and Bell produce commercial version of Gorrie's system for freezing beef. The frozen meat trade becomes more successful and stems the Malthusian revolution
	Cailletet produced a fog of liquid air, and Pictet a jet of liquid oxygen
1878	James Dewar duplicates the Cailletet/Pictet experiment before the Royal Institution
1879	The SS. <i>Strathaven</i> arrives in London carrying a well preserved cargo of frozen meat from Australia
	Linde founded the Linde Eismachinen
1897	Charles Tripler of NY produces 15 L/hr of liquid air using a 75 kW steam engine power source. Liquid air provides high-pressure gas to drive his air compressor and tripler is convinced he can make more liquid air than he consumes, the "surplusage" effect
1882	Jules Violle develops the first vacuum insulated flask
1883	Wroblewski and Olszewski liquefied both nitrogen and oxygen
1005	Vapor cooled shielding developed by Wroblewski and Olszewski
1884	Wroblewski produced a mist of liquid hydrogen
1891	Linde had put 12,000 domestic refrigerators in service.
	Dewar succeeds for the first time in liquefying hydrogen in a mist
1892	Dewar developed the silvered, vacuum-insulated flask that bears his name
1894	Dewar first demonstrated benefit of gas mixtures in J-T expansion Onnes first uses the word "cryogenics" in a publication
1895	Kammerlingh Onnes established the University of Leiden cryogenics laboratory Linde is granted the basic patent on air liquefaction
	First Hampson heat exchanger made for air liquefaction plants Hampson and Linde independently patent air liquefiers using Joule–Thomson expansion and recuperative cooling
1897	Dewar demonstrates the vacuum powder insulation
1898	Dewar produced liquid hydrogen in bulk, at the royal Institute of London
1890	Dewar improves upon the Violle vacuum flask by slivering both surfaces
1902	Claude developed an air liquefaction system using an expansion engine using leather seals, and established l'Air Liquide
	Reinhold Burger markets Dewar vessels under the name Thermos <sup>®</sup>
1007	I ripler (1897) files for bankruptcy after his "surplusage" is proven false
1907	Chercher and and a start in the use of the start of the s
1000	Claude produced neon as a by product of an air plant
1908	Onnes inqueried helium and received the Noble prize for his accomplishment
1910	Van der Waals receives Nobel prize for work on the critical region

**Table 1.2** Notable Events in the History of Cryogenics

(Continued)

Table 1.2	( <i>Continued</i> )
-----------	----------------------

20

1911	Onnes discovered superconductivity		
1912	First American made air liquefaction plant		
1913	Kammerlingh Onnes receives Nobel for work on liquid Helium		
1916	First commercial production of argon in the USA by the Linde Company		
1917	First natural gas plant produces gaseous helium		
1920	Commercial production of neon in France		
1922	First commercial neon production in the USA		
1926	Dr. Goddard fired the first cryogenically propelled rocket		
	Giauque and Debye independently discover the adiabatic demagnetization principle for producing temperatures much lower than 1 K		
1933	Magnetic cooling first produces temperatures below 1 K		
1934	Kapitza produces first expansion engine for making liquid helium		
	H. C. Urey receives the Nobel for his discovery of deuterium		
1936	P.J.W. debye receives Nobel prize for discoveries on heat capacity at low temperatures		
1937	Evacuated-powder insulation, originally tested by Dewar, is first used on a commercial scale in cryogenic storage vessels		
	First vacuum-insulated railway tank car built for liquid oxygen		
	Hindenburg Zeppelin crashed and burned at Lakehurst, NJ. The hydrogen burned but did not explode. Thirty-seven out of 39 passengers survived, making this disaster eminently survivable as far as air travel goes (63 out of 100 total passengers and crew survived). Nonetheless, hydrogen gains an extremely bad		
1042	reputation		
1942 1944	LNG tank in Cleveland OH fails killing 131 persons. LNG industry set back 25		
1947	Collins cryostat developed making liquid helium readily available for the first		
10/18	First 140 ton/day ovvgen system built in the USA		
1950	Emmanuel Maxwell receives Nobel prize for discovering the isotope effect in		
1750	superconductors		
1952	National Bureau of Standards Cryogenic Engineering laboratory built in Boulder, Colorado, including the first large-scale liquid hydrogen plant in the USA		
1954	First Cryogenic Engineering Conference held by NBS at its Boulder Laboratories		
1956	BCS theory of superconductivity proposed		
1957	Atlas ICBM tested, firs use in the USA of liquid oxygen-RP1 propellant Lee and Yang receive Nobel for upsetting the theory of parity		
1958	Multilayer cryogenic insulation developed		
1959	The USA space agency builds a tonnage liquid hydrogen plant at Torrance, CA		
1960	D.A. Glaser receives Nobel for his invention of the bubble chamber		
1961	Liquid hydrogen fueled Saturn launch vehicle test fired		
	R. L. Mossbauer receives Nobel for discoveries in radiation absorption		
1962	L. D. Landau awarded the Nobel Prize for discoveries in He <sup>3</sup>		
1968	L. W. Alvarez receives Nobel Prize for his work with liquid hydrogen bubble chambers		
1969	Liquid hydrogen fueled Saturn vehicle launched from Cape Canaveral, FL carrying Armstrong, Aldrin, and Collins to the moon		
1972	Bardeen, Cooper, and Schrieffer receive Nobel for the BCS theory of superconductivity		

(Continued)

1973	B. D. Josephson, I. Giaever, and L. Esaki awarded the Nobel prize for discovery
	of the Josephson Junction (tunneling supercurrents)
1978	Peter Kapitza receive the Nobel for the characterization of HeII as a superfluid
1987	J. G. Bednorz and K. A. Mueller awarded the Nobel Prize for discovering high-temperature superconductors
	Y-BA-Cu-O ceramic superconductors found
1996	D. Lee, D. D. Osheroff, and R. C. Richardson receive the Nobel prize of the discovery of superfluidity in helium-3
1997	S. Chu and Claude Cohen-Tannoudji awarded the Nobel for discovering methods to cool and trap atoms with lasers
1998	R. B. Laughlin, H. L. Stormer, and D. C. Tsui receive the Nobel for discovering a new form of quantum fluid excitations at extremely low temperatures
2001	E. Cornell, W. Ketterle, and C. Wieman awarded the Nobel for achieving the Bose–Einstein condensate at near absolute zero

Table 1.2 (	Continued)
-------------	------------

refrigerators are needed to maintain the necessary temperatures. Furthermore, the degree of insulation required is much more simple, and the vacuum requirements of liquid helium disappear.

#### **10. SCIENCE MARCHES ON**

Many Nobel laureates received their honors either because of work directly in cryogenics, or because of work in which cryogenic fluids were indispensable refrigerants. Table 1.1 provides an imposing list of such Nobel Prize winners.

Two examples from this list of Nobel laureates are considered to illustrate the application of cryogenics to education and basic research.

The first example involves Donald Glaser who invented the bubble chamber. Glaser recognized the principal limitation of the Wilson cloud chamber, namely that the low-density particles in the cloud could not intercept enough high-energy particles that were speeding through it from the beams of powerful accelerators. Glaser's first bubble chamber operated near room temperature and used liquid diethylether. To avoid the technical difficulties presented by such a complex target as diethylether, Prof. Luis Alvarez, of the University of California, devised a bubble chamber charged with liquid hydrogen. Since hydrogen is the simplest atom, consisting only of a proton and an electron, it interferes only slightly with the high-energy processes being studied with the giant accelerators, although it is readily ionized and serves quite well as the detector in the bubble chamber.

The first really large liquid-hydrogen bubble chamber was installed at the Lawrence Radiation Laboratory of the University of California and became operative in March 1959. A remark was made that this 72-in. liquid-hydrogen bubble chamber would be the equivalent of a Wilson cloud chamber one-half mile long. They could not really be equal, however, because the cloud chamber does not have the great advantage of utilizing the simplest molecules as the detector.

The second example chosen from the list of Nobel laureates that serves to link cryogenics to basic science is John Bardeen, who was cited for his work in
semiconductors, and more recently has worked in superconductivity. His exposition in 1957, of what is now known as the BCS theory of superconductivity, has helped make this field one of the most active research fields in physics in the last century.

Table 1.2 gives a chronology of some of the major events in the history of cryogenics.

# 1. INTRODUCTION

In the last half of the 19th century, roughly from 1850 to the turn of the century, the principal export of the United States was cotton. The second most important export by dollar volume was *ice*. Americans developed methods for harvesting, storing, and transporting natural ice on a global scale. In 1810, a Maryland farmer, Thomas Moore, developed an ice-box to carry butter to market and to keep it hard until sold. This early refrigerator was an oval cedar tub with an inner sheet of metal serving as a butter container that could be surrounded on four sides by ice. A rabbit skin provided the insulated cover. Moore also developed an insulated box for home use. It featured an ice container attached to the lid and a 6 cu ft storage space below. Ice harvesting was revolutionized in 1825 when Nathaniel J. Wyeth invented a horsedrawn ice cutter (see Fig. 2.1.) It was Wyeth's method of cutting blocks of similar size quickly and cheaply that made the bountiful supplies of natural ice resources of the United States available for food preservation. A steam-powered endless chain was developed in 1855 that could haul 600 tons of ice per hour to be stored. Wyeth and Tudor patented a means to prevent the ice blocks from freezing together by placing saw-dust between the layers. Uniform blocks reduced waste, facilitated transportation, and introduced ice to the consumer level (see Figs. 2.2 and 2.3).

The amount of ice harvested each year was staggering. In the winter of 1879– 1880, about 1,300,000 tons of ice was harvested in Maine alone, and in the winter of 1889–1890, the Maine harvest was 3 million tons. The Hudson River supplied about 2 million tons of ice per year to New York City during that period. Even that was not enough, for during those same years, New York City imported about 15,000 tons from Canada and 18,000 tons from Norway annually.

Ice changed the American diet. Fresh food preserved with ice was now preferred to food preserved by smoking or salting. Fresh milk could be widely distributed in the cities. By now, the people were accustomed to having ice on demand, and great disruptions of the marketplace occurred when ice was not available. Ice was, after all, a natural product, and a "bad" winter (a warm one) was disastrous to the marketplace and to the diet. It was time for the invention of machines to make ice on demand and free the market from dependence on the weather.

Machines employing air as a refrigerant, called compressed air or cold air machines, were appearing. They were based on the reverse of the phenomenon of heating that occurred when air was compressed, namely that air cooled as it expanded against resistance. This phenomenon of nature had been observed as early as the middle of the 18th century. Richard Trevithick, who lived until 1833 in



**Figure 2.1** Ice harvesting and storage in the 1850s. Accumulated snow was first removed with a horse-drawn ice plane. Then a single straight groove was made with a hand tool. The ice was marked off from this line into squares 22 in. on a side. Actual cutting was begun with Wyeth's invention and finished with hand saws. The uniform blocks of ice were pulled across the now open water to the lift at the icehouse. Here, they were stored under an insulation of straw or sawdust. The availability of a relatively dependable supply of ice all year, combined with uniformity of size of blocks, did much to create the market for ice.



**Figure 2.2** Delivering ice in New York, 1884. In this neighborhood, apparently, icemen did not enter the kitchen but sold their wares at the curb.



**Figure 2.3** Commercial ice delivery in New York, 1884. We see delivery to a commercial establishment, possibly a saloon. Though ice is available, the butcher a few doors down the street still allows his meat to hang unrefrigerated in the open air.

Cornwall, England, constructed engines in which expanding air was used to convert water to ice. In 1846, an American, John Dutton, obtained a patent for making ice by the expansion of air. The real development of the cold air machine, however, began with the one developed by John Gorrie of Florida and patented in England in 1850 and in the United States in 1851.

Later, we shall see how Gorrie's machine evolved into true cryogenics, not merely ice production. For now, however, in the late 1800s, it was possible to buy an ice-making machine for home use like that shown in Fig. 2.4. This primitive refrigerator had the same components as any refrigerator of today. It also followed exactly the same thermodynamic process as all of today's refrigerators.

All refrigerators involve exchanging energy (work, as the young lady in Fig. 2.4 is doing) to compress a working fluid. The working fluid is later expanded against a resistance, and the fluid cools (usually). Engineers have made it their job to determine how much cooling is produced, how much work is required for that cooling, and what kind of compressor or other equipment is required. More than that, we have made it our business to optimize such a cycle by trading energy for capital until a minimum cost is found. We can make any process more "efficient", that is, less energy-demanding, by increasing the size, complexity, and cost of the capital equipment employed. For instance, an isothermal compressor requires less energy to operate than any other kind of compressor. An isothermal compressor is also the most expensive compressor to build, because an infinity of intercooling stages are required for true isothermal compression.

As another example of trading energy costs for capital costs, consider the Carnot cycle (described later), which is the most thermodynamically efficient heat engine cycle possible. An essential feature of the Carnot engine is that all heat



**Figure 2.4** Home ice machine. Machines such as this were available from catalog centers in the late 1880s. The figure illustrates that energy (work) and capital equipment are at the heart of all cryogenic processes.

transfer takes place with zero  $\Delta T$  at the heat exchangers. As a consequence, a Carnot engine must have heat exchangers of infinite size, which can get pretty costly. In addition, the Carnot engine will never "get there" because another consequence of zero  $\Delta T$  is that an infinite amount of time will be required for heat transfer to take place.

Someone noted for all posterity: There once was a young man named Carnot Whose logic was able to show For a work source proficient There is none so efficient As an engine that simply won't go.

The science that deals with these trade-offs between energy and capital is *ther-modynamics*. Thermodynamics is about money. We need to predict how much a refrigerator will cost to run (the energy bill) and how much it will cost to buy (the capital equipment bill). Accordingly, our first job is to define *heat* and *work*, the energy that we must buy. *Work* is fairly easily defined as the product of a force and a displacement. Its symbolic representation takes many different forms, such as  $\int P \, dV$ , but it is always the product of an external force and the displacement that goes with that force. Heat is more troublesome to calculate. The driving force for heat,  $\Delta T$ , seems obvious and analogous to the *force* or *P* term of the *work* equation. But what is the equivalent *displacement* for heat? What gets moved, if there is such an analogy?

Carnot reasoned, by the flow of water, that there must be a flow of heat. He also reasoned that in the case of heat, something must be conserved, as energy itself is conserved (here he was right). Carnot discovered that the quantity that was conserved, and that was displaced, was not heat but rather the quantity Q/T. This led Carnot to the concept of *entropy*. In this book, *entropy* (S) is used to calculate heat (Q). That calculation is analogous to the one for work. Just as dW = P dV, likewise dQ = T dS. There are certainly more sophisticated implications of *entropy*, but for us, *entropy* is just a way to calculate how much heat energy is involved.

We need these ways to calculate heat and work because it is heat and work (energy) that we pay for to run the equipment. You will never see a work meter or a heat meter on any piece of cryogenic equipment. Instead it is a fact of nature that these two economically important quantities must be calculated from the thermodynamically important quantities, the things that we can measure: pressure (P), temperature (T), and density (actually, specific volume). Hence, we need two more tools.

One essential tool is an equation of state to tie pressure, volume, and temperature together.

The second essential tool to help us figure out the cost is the thermodynamic network that links not only P, V, and T together but also links all of the other thermodynamic properties (H, U, S, G, A,...—you know what I mean) together in a concise and consistent way. In real life, we usually measure pressure and temperature because it is possible to buy pressure gauges and thermometers and it is not possible to buy entropy or enthalpy gauges. Hence, we need a way to get from P and T to H and S. (The beautiful thermodynamic network that gets us around from P to T to heat and work is shown later in Fig. 2.7.) This thermodynamic network is the only reason we delve into partial differential equations, the Maxwell relations, and the like. The payoff is that we can go from easily measured quantities, pressure and temperature, to the hard-to-measure, but ultimately desired, quantities of *heat* and *work*. You might want to look at Fig. 2.7 now to discover a reason to plow through all the arcane stuff between here and there. Once we do get our hands on the thermodynamic network, we can calculate *heat* and *work* for any process, for any fluid, for all time.

We will start our cryogenic analysis with some definitions. Admittedly, this is a boring approach. However, it will ensure that we are all singing from the same sheet of music. We begin with nothing less than the definition of thermodynamics itself.

# 2. THERMODYNAMICS

Thermodynamics is built upon four great postulates (guesses), which are called, rather stuffily, the four laws of thermodynamics.

The second law was discovered first; the first law was discovered second; the third law is called the zeroth law; and the fourth law is called the third law. I am sorry to tell you that things do not get much better.

The *zeroth law* of thermodynamics just says that the idea of temperature makes sense.

The *first law* of thermodynamics is simply the conservation of energy principle. Inelegantly stated, the first law says that what goes into a system must either come out or accumulate. Undergraduates often call this the "checkbook law". If you can balance your checkbook, you can do thermodynamics.

The *second law* is the entropy principle. The second law is also a conservation equation, stating that in the ideal engine, entropy (S) is conserved. All real engines make entropy.

The *third law* just says that there is a temperature so low that it can never be reached.

These colloquial expressions of the four great principles of thermodynamics have a calming effect. We will not be able to quantify our analyses unless we use much more precise definitions and, expressly, the mathematical statements of these principles. That is the task we must now turn to.

Thermodynamics is concerned with energy and its transformations into various forms. The laws of thermodynamics are our concepts of the restrictions that nature imposes on such transformations. These laws are *primitive*; they cannot be derived from anything more basic. Unfortunately, the expressions of these laws use words that are also primitive; that is, these words are in general use (e.g., energy) and have no precise definition until we assign one. Accordingly, we begin our discussion of the fundamental concepts of thermodynamics with a few definitions.

**Thermodynamics:** Thermodynamics is concerned with the interaction between a system and its surroundings, the effect of that interaction on the properties of the system, and the flow of heat and work between the system and its surroundings.

**System:** Any portion of the material universe set apart by arbitrarily chosen but specific boundaries. It is essential that the system be clearly defined in any thermo-dynamic analysis.

Surroundings: All parts of the material universe not included in the system.

The definitions of *system* and *surroundings* are coupled. The system is any quantity of matter or region mentally set apart from the rest of the universe, which then becomes the surroundings. The imaginary envelope that distinguishes the system from the surroundings is called the *boundary* of the system.

**Property of the system, or state variable:** Any observable characteristic of the system, such as temperature, pressure, specific volume, entropy, or any other distinguishing characteristic.

**State of the system:** Any specific combination of all the properties of the system such as temperature, pressure, and specific volume. Fixing any two of these three properties automatically fixes all the other properties of a homogeneous pure substance and, therefore, determines the condition or *state* of that substance. In this respect, thermodynamics is a lot like choosing the proper size dress shirt for a gentleman. If you specify the neck size and sleeve length, the shirt size is defined. The size of a man's dress shirt is determined by two variables: neck size and sleeve length. A single-phase homogeneous thermodynamic system is defined by fixing any two thermodynamic variables. If you can pick out shirt size correctly, you can do thermodynamics.

**Energy:** A very general term used to represent heat, work, or the capacity of a system to do heat or work.

**Heat:** Energy in transition between a system and its surroundings that is caused to flow by a temperature difference.

**Work:** Energy in transition between a system and its surroundings. Work is always measured as the product of a force external to the system and a displacement of the system.

If there is no system displacement, there is no work. If there is no energy in transition, there is no work. Consider the following conundrum: It has been raining steadily for the last hour at the rate of 1 in. of rain per hour. How much rain is on the

ground? Answer: *none*. Rain is water in transition between heaven and earth. Once the water hits the earth, it is no longer rain. It may be a puddle or a lake, but it is not rain.

Likewise, *heat* and *work* are energy in transition between system and surroundings. Heat and work exist only while in transition. Once transferred, heat and work become internal energy, or increased velocity, or increased kinetic energy, but they are no longer heat and work. Heat and work cannot reside in a system and are not properties of a system.

Because heat and work are in transition, they have direction as well as magnitude, and there is a sign convention to tell us which way they are moving.

The convention among chemists and chemical engineers is:

Direction of energy flow	Sign convention
Heat into the system Heat out of the system Work into the system Work out of the system	<ul> <li>(+) Positive</li> <li>(-) Negative</li> <li>(-) Negative</li> <li>(+) Positive</li> </ul>

Thus, the expression Q - W is the algebraic sum of all the energy flowing from the surroundings into the system. Q - W is the net gain of energy of the system.

**Process:** The method or path by which the properties of a system change from one set of values in an initial state to another set of values in a final state. For example, a process may take place at constant temperature, at constant volume, or by any other specified method. A process for which Q=0 is called an adiabatic process, for instance.

**Cyclic process:** A process in which the initial state and final state are identical. The *Carnot cycle*, mentioned earlier, is such a cyclic process. We will now examine the Carnot cycle in the light of the preceeding definitions.

In 1800, there was an extraordinary Frenchman who was a statesman and government minister. His work was so important that he was known as the "organizer of victory of the French Revolution". Lazare Nicholas Marguerite Carnot (1753– 1823) was also an outstanding engineer and scientist. A century later, this glorious family tradition was carried on by his grandson, Marie François Sadi Carnot (1837–1894), another gentleman engineer, who served as the President of the Republic of France from 1887 to 1894, when he was assassinated.

The Carnot family member we are interested in is neither of these, but a cousin who lived between them. Nicholas Leonard Sadi Carnot (1796–1832), called "Sadi" by everyone, was very interested in steam engines. He wanted to build the most efficient steam engine of all to assist in military campaigns. Sadi needed the steam engine that required the least fuel for a given amount of work, thereby reducing the logistical nightmare of fueling the war engines.

He began by considering the waterwheel. He reasoned that it should be possible to hook two waterwheels together, one driven by falling water in the conventional way. The other, joined to the first by a common shaft, should be able to pick up the water spent by the first and carry it up to the headgate of the first. In this perfect, frictionless engine, one waterwheel should be able to drive the other forever. We know, as Sadi knew, that this is not possible because of the losses (friction) in the system. However, the idea led Sadi to the conclusion that the most efficient engine would be a *reversible* one, an engine that could run equally well in either direction. The perfect waterwheel could be driven by falling water in one direction or simply run in reverse to carry (pump) the water to the top again. A pair of such *reversible* engines could thus run forever. Anything less than a *reversible* engine would eventually grind to a halt. Hardly anyone paid any attention to Carnot and his seminal concept, and indeed, Carnot's work was further obscured by his early death.

Carnot's perfect abstraction was noticed, however, by the German physicist Rudolph Clausius and the Glaswegian professor of natural philosophy William Thomson. The principle of the conservation of energy was well established by this time. Crudely stated: the energy that goes into a system must either come out or accumulate. In the steady state, exactly the energy that goes into the engine must come out, regardless of the efficiency of the engine. Clausius and Thomson both saw in Carnot's work that a perfect engine would conserve energy like any other engine, but in addition, the quantity Q/T would also be conserved. In the perfect (reversible) engine,  $Q_{in}/T_{in} = Q_{out}/T_{out}$ . Not only is energy conserved (the first law) but also the quantity Q/T is conserved in the ideal engine.

This astonishing fact leads us to the concept of entropy, S. Entropy was defined then as now as  $S = Q_{rev}/T$  because of the remarkable discovery that the quantity Q/T, entropy, is conserved in the ideal (reversible) engine. We can summarize the work of Clausius, Thomson, and Carnot by saying that in an ideal engine,  $S_{in} = S_{out}$ ; in any real engine,  $S_{out} \ge S_{in}$ . We now have a concise description of the most efficient engine possible,  $S_{in} = S_{out}$ . All real engines, regardless of their intended product, produce entropy:  $S_{out} \ge S_{in}$  for any real engine.

This is the reason that the concept of reversibility is so important, and it leads to the following definition:

**Reversible process:** A process in which there are no unbalanced driving forces. The system proceeds from the initial state to the final state only because the driving forces in that direction exceed forces opposing the change by an infinitesimal amount. In short, no forces are wasted.

#### 2.1. Master Concepts

Thermodynamics is built upon experience and experimentation. A few master concepts have emerged, which may be stated as follows.

*Postulate 1.* There exists a form of energy, known as *internal energy U*, that is an intrinsic property of the system, functionally related to pressure, temperature, and the other *measurable* properties of the system. U is a property of the system, but is not *directly measurable*.

The second master concept is simply a conservation equation, known as the *first law of thermodynamics*:

*Postulate 2.* The *total energy* of any system and its surroundings is conserved.

A third postulate qualifies the first law by observing that not all forms of energy have the same quality, or availability for use (the concept of entropy).

*Postulate 3.* There exists a property called *entropy S*, which is an intrinsic property of the system that is functionally related to the *measurable* properties that characterize the system. For reversible processes, changes in this property can be calculated by

the equation

$$\mathrm{d}S = \mathrm{d}Q_{\mathrm{rev}}/T \tag{2.1}$$

where T is the absolute temperature of the system.

The first law of thermodynamics cannot be properly formulated without the recognition of internal energy U as a property. Internal energy is a concept. Likewise, the second law of thermodynamics can have no complete description without the recognition of entropy as a property. Entropy is also a concept, just as internal energy is a concept, but is usually much harder to grasp.

Abstract quantities such as internal energy U and entropy S are essential to the thermodynamic solution of problems. Accordingly, a necessary first step in thermodynamic analysis is to translate the problem into the terminology of thermodynamics. One of the real systems most often encountered in cryogenic engineering is the one described by pressure, temperature, and specific volume. These systems are called *PVT* systems and are composed of fluids, either liquids or gases or both. For such systems, yet another postulate is required.

*Postulate 4.* The macroscopic properties of homogeneous *PVT* systems in equilibrium states can be expressed as functions of pressure, temperature, and composition only.

This postulate is the basis for all the thermodynamic equations that will follow and has enormous utility. It is the basis for assuming the existence of an equation of state relating P, V, and T. Note that it neglects the effects of electric, magnetic, and gravitational fields and also neglects viscous shear and surface effects.

As mentioned, these postulates are *primitive*; they cannot be derived from anything more basic.

#### 2.2. The First Law of Thermodynamics

As stated above, the first law is a conservation equation: energy transferred to a system will be conserved as changes in properties of the system or changes in potentials of the system. That is, energy may be transferred or altered in form but never created or destroyed. Energy that enters a system must either come out of the system or accumulate (the checkbook principle):

Heat added to the system + Work done on the system

= Changes in internal energy U

+ Changes in potential and kinetic energy

or

$$Q - W = \Delta U + \Delta$$
(potential and kinetic energy) (2.2)

In Eq. (2.2), the term Q - W represents all the energy a system has received from its surroundings. This energy gained by the system is divided into two portions:

- 1. The increase in internal energy U within the system due to the composite effect of changes in the configuration and motion of all of its ultimate particles. This increment is represented by the term  $\Delta U$ .
- 2. The increase in potential and kinetic energy of the entire system due to changes in the position and motion of the system as a whole. This is

written as

$$\Delta(\text{PE} + \text{KE}) = \frac{mg\Delta Z}{g_c} + \frac{m\Delta v^2}{2g_c}$$
(2.3)

where *m* is the mass of the system,  $\Delta Z$  is the elevation of the system above a reference plane, *v* is the velocity of the system, *g* is the local acceleration of gravity, and  $g_c$  is the gravitational constant.

*Example 2.1.* Water is flowing at a velocity of 100 ft/s through a pipe elevated 250 ft above a reference plane. What are the kinetic energy (KE) and the potential energy (PE) of  $1 \text{ lb}_m$  of the water?

The work done on a body to increase its velocity leads to the kinetic energy concept. From the first law, the work done on the body to accelerate it is transformed into the kinetic energy of the body.

Work is defined as force times displacement, or

 $W = F \times l$ 

and

dW = Fdl for a constant force F

The force may be obtained from Newton's second law of motion,

$$F = \frac{ma}{g_c}$$

where m is the mass of the body, a is the acceleration, and  $g_c$  is a proportionality constant called the gravitational constant. In the American engineering system,

$$g_c = 32.174 \frac{(\mathrm{ft})(\mathrm{lb_m})}{(\mathrm{s}^2)(\mathrm{lb_f})}$$

Therefore,

$$\mathrm{d}W = \frac{ma}{g_c} \mathrm{d}l$$

By definition, acceleration is

$$a = \frac{\mathrm{d}v}{\mathrm{d}t}$$

where *v* is the velocity of the body. Hence,

$$\mathrm{d}W = \frac{m}{g_c} \frac{\mathrm{d}v}{\mathrm{d}t} \,\mathrm{d}l$$

or

$$\mathrm{d}W = \frac{m}{g_c} \frac{\mathrm{d}l}{\mathrm{d}t} \,\mathrm{d}v$$

Since the definition of velocity is

$$v = \frac{\mathrm{d}l}{\mathrm{d}t}$$

the expression for work becomes

$$\mathrm{d}W = \frac{m}{g_c} v \,\mathrm{d}v$$

This equation may now be integrated for a finite change in velocity from  $v_1$  to  $v_2$ :

$$W = \frac{m}{g_c} \int_{v_1}^{v_2} v \, \mathrm{d}v = \frac{m}{g_c} \left( \frac{v_2^2}{2} - \frac{v_1^2}{2} \right)$$

or

$$W = \frac{mv_2^2}{2g_c} - \frac{mv_1^2}{2g_c} = \frac{\Delta mv^2}{2g_c}$$

The quantity  $mv^2/2g_c$  was defined as the kinetic energy by Lord Kelvin in 1856. Thus,

$$KE = \frac{mv^2}{2g_c}$$
(2.4)

For the case given in the problem statement above,

Kinetic energy = 
$$(1 \text{ lb}_m) \left(100 \frac{\text{ft}}{\text{s}}\right)^2 \left(\frac{1}{2}\right) \left(\frac{1}{32.174} \frac{\text{s}^2 \text{ lb}_f}{\text{ft} \text{ lb}_m}\right)$$
  
= 155 ft lb<sub>f</sub>

Similarly, the work done on a body to change its elevation leads to the concept of potential energy.

If a body of mass *m* is raised from an initial elevation  $z_1$  to a final elevation  $z_2$ , an upward force at least equal to the weight of the body must be exerted on it, and this force must move through the distance  $z_2 - z_1$ . Since the weight of the body is the force of gravity on it, the minimum force required is given by Newton's second law of motion:

$$F = \frac{1}{g_c}ma = \frac{1}{g_c}mg$$

or

where g is the local acceleration of gravity and  $g_c$  is as before. The minimum work required to raise the body is the product of this force and the change in elevation:

$$W = F(z_2 - z_1) = m \frac{g}{g_c} (z_2 - z_1)$$

$$W = mz_2 \frac{g}{g_c} - mz_1 \frac{g}{g_c} = \Delta \left(\frac{mzg}{g_c}\right)$$

The work done on a body in elevating it is said to produce a change in its *potential energy* (PE), or

$$W = \Delta PE = \Delta \frac{mzg}{g_c}$$

Thus, potential energy is defined as

$$PE = mz \frac{g}{g_c}$$
(2.5)

This term was first proposed in 1853 by the Scottish engineer William Rankine (1820–1872).

For the problem statement above,

Potential energy = 
$$(1 \text{ lb}_m)(250 \text{ ft}) \left(32.174 \frac{\text{ft}}{\text{s}^2}\right) \left(\frac{1}{32.174} \frac{\text{s}^2 \text{ lb}_f}{\text{ft} \text{ lb}_m}\right)$$
  
= 250 ft lb<sub>f</sub>

Potential energy and kinetic energy are obvious mechanical terms. The energy put into a system may be stored in elevation change or in velocity change as well as in internal energy U by way of property changes.

The internal energy U represents energy stored in the system by changes in its properties T, P, V, etc.  $\Delta U$  is a composite effect of changes in the motion and configuration of all of the ultimate particles of a system.

It is essential to note that the left-hand side of Eq. (2.2) describes a system– surroundings interaction, while the right-hand side describes properties of the system alone. This is a very valuable aspect of the first law equation, for it permits the calculation of system–surroundings interactions (heat and work) from changes in system properties only. Some of the consequences of this attribute of the first law equation are discussed below.

As stated earlier, work is a system–surroundings interaction—energy in transit between the system and surroundings, a precise kind of energy that crosses the system boundary. Therefore, work must always have two components: an external (surroundings) force and an internal (system) displacement. Work is always

 $F_{\text{external}} \times X_{\text{system}}$ 

where X is the system displacement.

For fluids, work is always

 $P_{\text{external}} \times V_{\text{system}}$ 

Only in the reversible case is  $P_{\text{external}} = P_{\text{internal}}$ . Then, and only then, may the P of the system be substituted for  $P_{\text{external}}$  and equations of state be used to relate P and V.

Because the left-hand side of Eq. (2.2) involves a system–surroundings interaction, questions of *path* come into play (e.g., adiabatic, reversible, constant external pressure, etc.). Indeed, the path must always be specified for calculations involving the left-hand side of Eq. (2.2), i.e., heat and work. In thermodynamics, it is essential to distinguish between quantities that depend on path and those that do not. Indeed, we commonly make this distinction in ordinary affairs. For instance, the straight-line distance between Denver and Los Angeles is a fixed quantity, a property. On the other hand, other quantities for an auto-mobile trip between Denver and Los

Angeles—miles traveled, miles per gallon consumed, etc.—depend very much on the path.

As stated, the right-hand side of Eq. (2.2) describes attributes of the system only and contains properties and potentials of the system only. Thus, it can always be evaluated from system properties or potentials alone without considering the surroundings. The question of path is simply irrelevant, because there is no system–surroundings interaction to be found on the right-hand side of the first law statement.

It is a constant goal of thermodynamics to evaluate system–surroundings interactions (e.g., heat and work) in terms of properties and potentials of the system alone. The essence of the first law concept is (a) that it is a conservation equation and (b) that a system–surroundings interaction can be expressed as a function of system parameters only.

The first law is valid for all systems under all cases, as written in Eq. (2.2). There are numerous special cases, and some of the more important will now be considered.

# 2.2.1. Open System—the Flow Case

One special case of the first law of thermodynamics is the "open" system, or the flow case. For a flow system such as the one shown in Fig. 2.5, the first law can be stated as

$$Q-W = \Delta U + rac{g}{g_c}\Delta Z + rac{\Delta v^2}{2g_c}$$

In this case the system is the element of fluid, and

$$W = W_{\rm s} + W_1 + W_2$$

where  $W_s$  is the shaft work by pump,  $W_1$  the work done by surroundings on system (element of fluid) pushing it past boundary 1 and  $W_2$  the work done by system on surroundings as element of fluid emerges.

Since pressure is the force per unit area,  $F_1$  becomes

 $F_1 = P_1 A_1$ 



Figure 2.5 Open thermodynamic system—the flow case.

and the distance  $l_1$  through which  $F_1$  acts is

$$l_1 = \frac{V_1}{A_1}$$

where  $V_1$  is the specific volume of element fluid and  $A_1$  the cross-sectional area of pipe.

Therefore,  $W_1 = F_1 P_1$  becomes

$$W_1 = P_1 A_1 \left(\frac{V_1}{A_1}\right) = P_1 V_1$$

Likewise,

$$W_2 = P_2 A_2 \left(\frac{V_2}{A_2}\right) = P_2 V_2$$

and the total work, W, is

 $W = W_{\rm s} + P_2 V_2 - P_1 V_1$ 

The first law, as written above, becomes for this special case

$$Q - (W_{s} + P_{2}V_{2} - P_{1}V_{1}) = \Delta U + \frac{g}{g_{c}}\Delta Z + \frac{\Delta v^{2}}{2g_{c}}$$
$$Q - W_{s} = \Delta U = \frac{g}{g_{c}}\Delta Z + \frac{\Delta v^{2}}{2g_{c}} + P_{2}V_{2} - P_{1}V_{1}$$
$$= U_{2} + P_{2}U_{2} - U_{1} - P_{1}V_{1} + \frac{\Delta v^{2}}{2g_{c}} + \Delta Z \frac{g}{g_{c}}$$

which defines the enthalpy H as

$$H \equiv U + PV \tag{2.6}$$

Then,

$$Q - W_{\rm s} = H_2 - H_1 + \frac{\Delta v^2}{2g_c} + \Delta Z \frac{g}{g_c}$$

or

$$Q-W_{
m s}=\Delta H+rac{\Delta v^2}{2g_c}+\Delta Zrac{g}{g_c}$$

If velocity and elevation changes are negligible, then  $Q - W_s = \Delta H$ . This is the flow system analog of the first law for closed systems.

Consideration of other special cases of the first law leads to other auxiliary functions, discussed below.

## 2.2.2. The Constant-Volume Case

The first law,  $Q - W = \Delta U$ , can always be written in differential form because no path is involved in differential notation:

$$\mathrm{d}Q - \mathrm{d}W = \mathrm{d}U$$

36

But  $dW = P_{ext}dV$ , and since dV = 0 for constant volume,

$$\mathrm{d}Q = (\mathrm{d}U)_V$$

Differentiating with respect to temperature suggests the function

$$\left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_{V} = \left(\frac{\mathrm{d}U}{\mathrm{d}T}\right)_{V} \equiv C_{V}$$

which is the definition of heat capacity at constant volume.

# 2.2.3. The Constant-Pressure Case

The first law in differential form can be combined with the expression for work under constant pressure,  $dW = P_0 dV$ , to yield

$$\mathrm{d}Q - \mathrm{d}W = \mathrm{d}U$$

Thus,

 $\mathrm{d}Q = P_0\mathrm{d}V + \mathrm{d}U$ 

where  $P_0 =$  the constant system pressure. Rearranging gives

$$Q_P = P_0(V_2 - V_1) + \Delta U$$
  
=  $P_0V_2 - P_0V_1 + U_2 - U_1$   
=  $(P_0V_2 + U_2) - (P_0V_1 + U_1)$ 

and since  $P_0 = P_2 = P_1 = \text{constant}$ , this may be rewritten as

 $Q_P = (P_2 V_2 + U_2) - (P_1 V_1 = U_1)$ 

which, from the definition of enthalpy,  $H \equiv U + PV$ 

 $Q_P = H_2 - H_1 = \Delta H$ 

Thus, at constant pressure,

 $Q = (\Delta H)_P$ 

Differentiating this expression with respect to temperature suggests the function

$$\left(\frac{\mathrm{d}Q}{\mathrm{d}T}\right)_P = \left(\frac{\mathrm{d}H}{\mathrm{d}T}\right)_P \equiv C_P$$

which is the definition of heat capacity at constant pressure.

# 2.3. The Second Law of Thermodynamics

Another master concept, the second law, comes about from observing that Q and W do not have the same "quality". For instance,

- 1. W is highly ordered and directional.
- 2. Q is less versatile.
- 3. W can always be completely converted to Q regardless of the temperature, but not vice versa.
- 4. Q can flow only from  $T_{\text{hot}}$  to  $T_{\text{cold}}$ .

Q has a quality as well as a quantity, and that quality depends on the temperature. Also, the effect of adding Q to a system is always to change the properties of the system, so there must be a *property change* that describes the addition of Q.

We postulate a property in thermodynamics to describe these observations that meets the following qualitative requirements:

- 1. The addition of Q causes a property change in the system.
- 2. The way (path) in which Q is added fixes the magnitude of the property change.
- 3. Adding Q at a lower temperature causes a greater change than adding the same amount of Q at a higher temperature.

Thus, we invent a property of the system to fit these three criteria, namely entropy, S (see Eq. (2.1)):

$$S = \frac{Q_{\rm rev}}{T}$$

or

$$Q_{\rm rev} = T\Delta S$$

Since Q is not a property, its path must be specified, and  $Q_{rev}$  is chosen to complete the definition.

Thus, we have developed qualitatively Postulate 3, which was stated earlier: there exists a property called *entropy S*, which is an intrinsic property of a system that is functionally related to the measurable coordinates that characterize the system. For a reversible process, changes in this property are given by

$$\mathrm{d}S = \frac{\mathrm{d}Q_{\mathrm{rev}}}{T}$$

The definition of entropy,  $Q_{rev} = T\Delta S$ , can always be written in differential form because neither reversibility nor any other path has any significance in differential notation:

$$\mathrm{d}Q = T\,\mathrm{d}S$$

and hence the first law,

$$U = Q - W$$

becomes in differential form, for all cases and for all substances,

$$dU = T \, dS - P \, dV \tag{2.7}$$

This is a universal relationship, just like the first law. One can always write the first law in this differential form for all cases. Although derived for a reversible process, Eq. (2.7) relates properties only and is valid for any change between equilibrium states in a closed system. The question of reversibility/irreversibility has no significance to Eq. (2.7) because (a) the concept of path has no bearing on any equation written in differential form and (b) the equation dU = T dS - P dV contains properties of the system only. *Path* is a concept relevant to system–surroundings interactions, and "surroundings" are completely absent from this description of the system alone.

Entropy is a property of the system that is dependent on the configuration of all the ultimate particles that make up the system. A system in which all the ultimate particles are arranged in the most orderly manner possible has an entropy of zero. As the arrangement within the system is changed from an ordered to a more disordered or more random state, the entropy of the system increases.

The addition of heat to a system causes an increase in scattering and disorder among all the particles within the system, in other words, an increase in entropy.

If heat is added during a reversible process, this increase in entropy is related to the heat added by

$$Q_{\rm rev} = \int T \,\mathrm{d}S$$

If heat is transferred to the system during an irreversible process, then

$$\int T \, \mathrm{d}S > Q$$

or

$$\int T \,\mathrm{d}S = Q + \mathrm{lost} \,\,\mathrm{work}$$

The lost work is energy that might have done useful work but is dissipated instead, causing unnecessary randomness and disorder within the system.

The second law can be stated formally as follows.

*Second law of thermodynamics.* The entropy change of any system and its surroundings, considered together, is positive and approaches zero for any process that approaches reversibility.

The second law of thermodynamics is a conservation law only for reversible processes, which are unknown in nature. All natural processes result in an increase in total entropy. The mathematical expression of the second law is simply

 $\Delta S_{\text{total}} \geq 0$ 

where the label "total" indicates that both the system and its surroundings are included. The equality applies only to the limiting case of a reversible process.

# 2.4. Clausius Inequality and Entropy

In 1824, Nicholas Leonard Sadi Carnot proposed a heat power cycle composed of the following reversible processes shown in Fig. 2.6.

- 1. Isothermal reversible expansion and absorption of heat  $Q_1$  at temperature  $T_1$  (a-b).
- 2. Isentropic (adiabatic, reversible) expansion to  $T_2$  (b–c).
- 3. Isothermal reversible compression and rejection of heat  $Q_2$  at  $T_2$  (c-d).
- 4. Isentropic compression back to temperature  $T_1$  (d–a).

Since the energy change of the system for the complete cycle must be zero,

$$\Delta U_{\rm cycle} = 0 = Q_1 - Q_2 - W$$



Figure 2.6 Carnot's reversible heat power cycle.

or

$$Q_1 - Q_2 = W$$

where W is the net work, which is the difference between the work produced in the expansion process (b–c) and the work required in the compression process (d–a). Also, the absolute values of  $Q_1$  and  $Q_2$  are used, temporarily abandoning the usual sign convention.

The efficiency of this reversible cycle is

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

since  $Q_1 = T_1 \Delta S$  and  $Q_2 = T_2 \Delta S$ 

The efficiency of the Carnot engine can be expressed in terms of the temperature of the heat reservoirs alone:

$$\eta = \frac{T_1 - T_2}{T_1}$$

Carnot stated (and proved) the following principles, which are known today as the *Carnot principles*:

- 1. No engine can be more efficient than a reversible engine operating between the same high-temperature and low-temperature reservoirs. Here the term "heat reservoir" is taken to mean either a heat source or a heat receiver or sink.
- 2. The efficiencies of all reversible engines operating between the same constant-temperature reservoirs are the same.
- 3. The efficiency of a reversible engine depends only on the temperatures of the heat source and heat receiver.

The two equations for the efficiency of the Carnot cycle can be combined to yield

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} = \left(1 - \frac{T_2}{T_1}\right)$$

or

$$W = Q_1 \left( 1 - \frac{T_2}{T_1} \right)$$

But

$$W = Q_1 - Q_2$$

Therefore,

$$Q_1 - Q_2 = Q_1 \left( 1 - \frac{T_2}{T_1} \right)$$

which reduces to

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

or  $S_1 = S_2$ , which is to repeat that entropy is *conserved* in a reversible engine.

In 1848, Lord Kelvin (William Thomson of Glasgow) derived a temperature scale based on the above equation, independent of the thermodynamic substance employed in the cycle. He defined the scale such that

$$\frac{T_1}{T_2} = \frac{Q_1}{Q_2}$$

where  $Q_1$  is the heat received by a Carnot engine from a source at temperature  $T_1$  and  $Q_2$  is the heat rejected to a receiver at temperature  $T_2$ . One advantage of the absolute scale is the absence of negative temperatures.

Clausius noted that the Kelvin equation could be rearranged to give

$$\frac{Q_1}{T_1} = \frac{-Q_2}{T_2}$$
 or  $\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$ 

Here, the usual sign convention is used and the minus sign with  $Q_2$  denotes that heat is leaving the system. This equation indicates that the change in the quantity Q/T around a reversible or Carnot cycle is zero. Clausius extended this relationship to embrace all cyclic processes by stating that the cyclic integral of  $\delta Q/T$  is less than zero or in the limit equal to zero; thus,

$$\oint \frac{\delta Q}{T} \le 0$$

This equation is now known as the *inequality of Clausius*.

It can be proved that the cyclic integral of  $\delta Q/T$  is equal to zero for all reversible cycles and less than zero for all irreversible cycles. Since the summation of the quantity  $\delta Q/T$  for a reversible cycle is equal to zero, it follows that the value of the integral of  $\delta Q/T$  is the same for any reversible process between states 1 and 2 of a system and thus is a property of the system. It is this proof that gives credence to Postulate 3, that there is a property called entropy that is defined as the ratio of heat transferred during a reversible process to the absolute temperature of the system, or mathematically,

$$\mathrm{d}s = \left(\frac{\delta Q}{T}\right)_{\mathrm{rev}}$$

Entropy, since it is a property, is especially useful as one of the coordinates when representing a reversible process graphically.

#### 2.5. The Maxwell Relations

We are now in a position to construct a complete thermodynamic property network and develop the Maxwell relations. The purpose is to develop a set of property functions (also known as *state functions* or thermodynamic functions) that will enable us to calculate any thermodynamic property change (e.g.,  $\Delta S$ ,  $\Delta H$ ,  $\Delta U$ ) for any substance for any process.

By definition, H = U + PV and

$$\mathrm{d}H = \mathrm{d}U + P\,\mathrm{d}V + V\,\mathrm{d}P$$

or

 $\mathrm{d}U = \mathrm{d}H = P\,\mathrm{d}V - V\,\mathrm{d}P$ 

This form of U may be substituted into the first law in differential form:

$$dU = T \, dS + P \, dV \tag{2.8}$$

to yield

$$dH = T \, dS + V \, dP \tag{2.9}$$

It can easily be shown that for a reversible flow process,

 $-W_{\rm max} = H - Q_{\rm rev}$ 

or

 $-\mathrm{d}W = \mathrm{d}H - T\,\mathrm{d}S$ 

This form of the work available from a reversible flow process suggests the function

$$G = H - TS \tag{2.10}$$

which is the definition of *Gibbs free energy*. This can likewise be substituted into the differential form of the first law to yield

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P\tag{2.11}$$

Similarly, the maximum work for a closed reversible process is

$$-W_{\rm max} = \Delta U - Q_{\rm rev}$$

or

$$-\mathrm{d}W = \mathrm{d}U - T\,\mathrm{d}S$$

which suggests another new function,

$$A = U - TS \tag{2.12}$$

which is known as the *Helmholtz free energy*. If this is likewise substituted into the first law in differential form, we have

$$\mathrm{d}A = S\,\mathrm{d}T - P\,\mathrm{d}V\tag{2.13}$$

We have thus defined the *state functions*, functions of the properties of a system that, under various conditions, can relate changes in the properties of the system to the heat and work transferred between it and the surroundings. Since these functions or potentials are functions only of the properties of the system, they can be expressed

as exact differentials. Thus, changes in these functions depend only on the initial and final states of the system and not on the method or path by which the change takes place. These functions are

U = Q - W	Internal energy
H = U + PV	Enthalpy
G = H - TS	Gibbs free energy
A = U - TS	Helmholtz free energy

The four state functions written in differential form are

$$dE = T \, dS - P \, dV \tag{Eq. 2.8}$$

$$dH = T \, dS + V \, dP \tag{Eq. 2.9}$$

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P\tag{Eq. 2.11}$$

$$dA = S dT - P dV \tag{Eq. 2.13}$$

It would be imprecise to stop with the impression that these four state functions are derived from considering the maximum possible work connected with a reversible process. Such a consideration only suggests the function. New thermodynamic functions such as H, G, and A cannot in general be defined by the random combination of variables. As a minimum, dimensional consistency is required. Instead, a standard mathematical method exists for the systematic definition of the desired functions; this is the *Legendre transformation*. The functions for G, H, and A are in fact Legendre transformations of the fundamental property relation of a closed PVT system, dU = TdS - PdV.

A consequence of the Legendre transformation is that the resulting expressions for G, H, and A are exact differential equations with the following special property:

If z = f(x, y) and dz = Mdx + Ndy, then the property of exactness is that

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

Applying this property of exact differential equations to the four equations above yields the following Maxwell relations:

$$\left(\frac{\partial T}{\partial V}\right)_{S} = -\left(\frac{\partial P}{\partial S}\right)_{V}$$
(2.14)

$$\left(\frac{\partial T}{\partial P}\right)_{S} = \left(\frac{\partial V}{\partial S}\right)_{P} \tag{2.15}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{2.16}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{2.17}$$

The last two are among the most useful, because they relate entropy changes to an equation of state.

The development of many of these relations is shown in Fig. 2.7, as proposed by Dr. A. J. Kidnay of the Colorado School of Mines.





# 2.6. Equations of State

It is evident from the preceding discussion that thermodynamics provides a multitude of equations inter-relating the properties of substances. Given appropriate data, thermodynamics allows the development of a complete set of thermodynamic property values from which one can subsequently calculate the heat and work effects of various processes. *PVT* data are among the most important and are concisely given by equations of state.

The simplest equation of state is the *ideal gas law*:

$$\frac{PV}{RT} = 1 \tag{2.18}$$

The ideal gas law is useful for calculating limiting, low-pressure, cases; for defining the ideal gas thermodynamic temperature scale; and for calculating so-called residual properties; but it fails to predict the existence of the liquid state.

The ideal gas law, with all of its shortcomings, is nonetheless very useful and is found at the core of all other equations of state. It is fun to develop from mechanics. Doing so shows us that temperature is a direct measure of kinetic energy and that pressure is kinetic energy per unit volume.

## 2.6.1. Deriving the Ideal Gas Law

The requisites for an ideal gas are that the molecules occupy zero volume (or negligible volume compared to the total available) and that there be no interactions (forces) between molecules.

Consider *n* molecules of an ideal gas confined in a volume  $V^{t}$ . We want to find the pressure, i.e., the force per unit area, exerted on a confining wall. Force is the time rate of change of momentum, so we want to find that rate



The molecules are in random motion. Their velocity, a vector, can be resolved into three components. Take one component normal to the wall. Since the motion is random, on the average, one-third of the velocities are normal to the wall and half of those, one-sixth of the total, are moving toward the wall at any time (the other half are moving away from the wall).

The total number of molecules in the small box shown in the figure is the number per unit volume,  $n/V^{t}$ , times the volume A dL. One-sixth of that number is moving toward the wall and will strike the wall in the time dt that it takes to travel the distance dL at the average velocity, u = dL/dt. Thus, the rate at which molecules strike the wall is

$$\frac{1}{6} \left(\frac{n}{V^{t}}\right) A \, \mathrm{d}L\left(\frac{1}{\mathrm{d}t}\right) = \frac{1}{6} \left(\frac{n}{V^{t}}\right) A \, \mathrm{d}L\left(\frac{u}{\mathrm{d}L}\right) = \frac{1}{6} \left(\frac{n}{V^{t}}\right) A u$$

When molecules strike the wall, their velocity is reversed. So the total change in velocity is 2u. The rate of change of momentum is the rate of striking the wall times the mass per molecule (i.e., molecular weight times the change in velocity, 2u). Thus,

$$F = \frac{1}{6} \left(\frac{n}{V^{t}}\right) Au(M)(2u) = \frac{1}{3} \left(\frac{Mn}{V^{t}}\right) Au^{2}$$

and the pressure is

$$P = \frac{F}{A} = \frac{1}{3} \left( \frac{Mn}{V^{t}} \right) u^{2}$$

The ideal gas law is  $P = (n/V^{t}) RT$ ; thus,

$$\frac{1}{3}Mu^2 = RT \quad \text{or} \quad \frac{Mu^2}{2} = \frac{3}{2}RT$$

where  $Mu^2/2$  is the average kinetic energy per mole. Thus, we have shown that for an ideal gas the kinetic energy is directly proportional to the absolute temperature. Or, put another way, temperature is a direct measure of kinetic energy. Notice also that pressure is equal to kinetic energy per unit volume.

This short derivation also provides some insight into the universal gas constant R. R is the chemist's version of Boltzmann's constant k. R is in units per mole, and k is in units per molecule. Both R and k are scaling factors between temperature and energy. For physicists, E = kT. For chemists, it is PV = RT, where the product PV is energy. Several values of R are given in Table 2.1.

We have already defined the heat capacities  $C_v$  and  $C_p$ . The ideal gas derivation can also breathe some life into these two important quantities. Heat capacity describes the ability of some substance to "soak up" energy.

Consider the molecules of a monatomic ideal gas. The only way a monatomic gas can soak up energy is to increase in kinetic energy. That is, the only way a monatomic ideal gas can "contain" energy (short of energies large enough to affect electronic or nuclear changes) is by the motion of its molecules—translational kinetic energy. Thus, if energy is added to a box of such molecules at constant volume, the change in their internal energy will be

$$dU = d(\text{kinetic energy}) = d((3/2)RT) = (3/2)RdT$$

At constant volume,  $dU = C_V dT$ , therefore  $C_V = (3/2) R$  for a monatomic ideal gas. If energy is added at constant pressure, the volume will change. Work is done when the volume changes. The work is P dV, due to pushing back the surroundings at the same pressure, P, as the system. The total energy added is the change in internal energy plus the work (dU + P dV). This quantity equals dH (at constant P), and  $dH = C_P dT$  (at constant P). So,

$$\mathrm{d}H = C_P \,\mathrm{d}T = \mathrm{d}U + P \,\mathrm{d}V = C_V \,\mathrm{d}T + R \,\mathrm{d}T = (C_V + R) \,\mathrm{d}T$$

Thus,  $C_P = C_V + R$ . This is true for any ideal gas (monatomic or not, because the work expression is always the same).

For polyatomic molecules, the internal energy includes the translational kinetic energy, but the molecules also can "soak up" energy in the form of rotation and vibration about their bonds. Polyatomic molecules thus have greater  $C_V$  (and  $C_P$ )

Temp. unit	Pressure unit	Volume unit	Energy unit	R per gram mol
K			Calorie	1.9872
K	atm	cm <sup>3</sup>		82.057
K	atm	L		0.082054
K	mmHg	L		62.361
K	bar	L		0.08314
K	kg/cm <sup>2</sup>	L		0.08478
				R per lb mol
°R			Btu (IT)	1.986
°R			hphr	0.0007805
°R			kW hr	0.0005819
°R	atm	cu ft		0.7302
°R	in. Hg	cu ft		21.85
°R	mmHg	cu ft		555.0
°R	psia	cu ft		10.73
	psfa	cu ft	ft lb	1545.0
Κ	atm	cu ft		1.314
Κ	mmHg	cu ft		998.9

**Table 2.1** Values of the Gas Constant R for 1 mol of Ideal Gas

Selected values from API Research Project 44:

Ice point =  $0^{\circ}$ C = 273.16 K = 491.69°R.

Gram molar volume of ideal gas at 1 atm and  $0^{\circ}C = 22,414.6 \text{ cm}^3 = 22.4140 \text{ L}$ . Pound molar volume of ideal gas at 1 atm and  $32^{\circ}F = 359.05 \text{ cu}$  ft. 1 atm = 760 mmHg = 29.921 in. Hg = 14.696 psia.

1 hp = 550 ft lb/s = 745.575 W (IT).

1 cal = 41833 J (IT).

1.8 Btu/lb = 1.0 IT cal/g = 1.000657 cal/g.

than do monatomic molecules. As a first approximation,  $C_V$  increases by R for each additional atom in the molecule. This is a consequence of the principle of equipartion of energy: the value of  $C_V$  increases by (1/2)R for each additional mode by which energy can be soaked up (three translational modes plus one rotational and one vibrational per bond formed). This holds well for diatomic molecules  $[C_V = (5/2)R, C_P = (7/2)R]$ , but as more atoms are added it does not work so well. The vibrational modes and rotational modes are not completely independent in more complex molecules.

The molecules of real gases do occupy a volume of their own, and there is an attraction among them, the intermolecular force. The equation of state for a real gas will therefore contain the ideal gas law as a first approximation and add other terms to account for the volume of the molecules and the potential between the molecules. These *other terms* express the nonideality of real gases. We need these terms, not only for accuracy but also to explain why some gases cool as they expand and others do not. Without the nonideality expressed by these terms, there would be no change in temperature upon expansion. Ideal gases have a zero Joule–Thomson coefficient.

It is easy to find the ideal gas law in the virial equation of state.

The *virial equation of state* is extremely powerful and can be written in two forms.

1. As an expansion in volume (V) or density ( $\rho$ ):

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots$$
(2.19)

or

$$\frac{PV}{RT} = 1 + B\rho + C\rho^2 + \cdots$$
(2.20)

2. As an expansion in pressure:

$$\frac{PV}{RT} = 1 + B'P + C'P^2 + \cdots$$
 (2.21)

The virial coefficients (B, C, ...) can be calculated from first principles (two-body interactions, three-body interactions, etc.) and are functions of temperature only.

Generalized or corresponding state forms of the equation of state are also useful:

$$\frac{PV}{RT} = Z, \qquad Z = Z(T_{\rm r}, P_{\rm r}) \tag{2.22}$$

where Z is the compressibility factor and  $T_r$  and  $P_r$  are the reduced temperature and pressure, e.g.,  $T_r = T/T_c$ . T is the system temperature, and  $T_c$  is the critical temperature of the system component.

Another useful generalized equation of state is the three-parameter corresponding states form employing the acentric factor  $\omega$ ,

$$Z = f(T_{\rm r}, P_{\rm r}, \omega) \tag{2.23}$$

where  $\omega$  is a tabulated parameter for a specific substance.

Several of the more common equations of state are shown in Table 2.2.

The values of  $\Delta S$ ,  $\Delta H$ ,  $\Delta E$ , etc., can now be calculated for any process for any substance according to the following scheme.

**Step 1.** Choose a pair of coordinates from *P*, *T*, and *V*, for example, P-T, T-V, or P-V. The problem statement is useful; use what is given. If the process is isothermal or isobaric, choose *T* (or *P*) as one of the pair, because it is constant.

The P-T pair is commonly chosen (but any two will do for homogeneous systems of a pure component), as P and T are the most commonly measured variables. Step 2. Write the total differential in terms of the pair chosen, e.g.,

$$S = f(P, T)$$
  
$$dS = \left(\frac{\partial S}{\partial T}\right)_{P} dT + \left(\frac{\partial S}{\partial P}\right)_{T} dP$$
  
(2.24)

**Step 3.** Evaluate the partial differential coefficients from the basic Maxwell relations. For example, evaluate the first coefficient,  $(\partial S/\partial T)_P$ . Because this coefficient involves an entropy term (S) that changes with T at constant P, it is likely that H will be involved.

From the definition of dH,

 $\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}P$ 

Van der Waals:  

$$\binom{p + \frac{a}{\hat{V}^2}}{(\hat{V} - b)} = RT$$
Lorenz:  

$$p = \frac{RT}{\hat{V}^2}(\hat{V} + b) - \frac{a}{\hat{V}^2}$$
Dieterici:  

$$p = \frac{RT}{\hat{V} - b}e^{-a/\hat{V}RT}$$
Berthelot:  

$$RT = a$$

$$p = \frac{KT}{\widehat{V} - b} - \frac{u}{T\widehat{V}^2}$$

Redlich-Kwong:

$$\begin{bmatrix} p + \frac{a}{T^{1/2}\widehat{V}(\widehat{V} + b)} \end{bmatrix} (\widehat{V} - b) = RT$$
$$a = 0.4278 \frac{R^2 T_c^{2.5}}{p_c}$$
$$b = 0.0867 \frac{RT_c}{p_c}$$

Onnes:

$$p\widehat{V} = RT\left(1 + \frac{B}{\widehat{V}} + \frac{C}{\widehat{V}^2} + \cdots\right)$$
  
Holborn:  
$$p\widehat{V} = RT(1 + B'p + C'p^2 + \cdots)$$

Beattie-Bridgeman:  

$$p\widehat{V} = RT + \frac{\beta}{\widehat{V}} + \frac{\gamma}{\widehat{V}^{2}} + \frac{\delta}{\widehat{V}^{3}}$$

$$\beta = RTB_{o} - A_{o} - \frac{Rc}{T^{2}}$$

$$\gamma = -RTB_{o}b + aA_{o} - \frac{RB_{o}c}{T^{2}}$$

$$\delta = \frac{RB_{o}bc}{T^{2}}$$
Benedict-Webb-Rubin:  

$$p\widehat{V} = RT + \frac{\beta}{\widehat{V}} + \frac{\sigma}{\widehat{V}^{2}} + \frac{\eta}{\widehat{V}^{4}} + \frac{\omega}{\widehat{V}^{5}}$$

$$\beta = RTB_{o} - A_{0} - \frac{C_{o}}{T^{2}}$$

$$\sigma = bRT - a + \frac{c}{T^{2}} \exp\left(-\frac{\gamma}{\widehat{V}^{2}}\right)$$

$$\eta = c\gamma \exp\left(-\frac{\gamma}{\widehat{V}^{2}}\right)$$
Peng-Robinson:  

$$p = \frac{RT}{\widehat{V} - b} - \frac{a\alpha}{\widehat{V}(\widehat{V} + b) + b(\widehat{V} - b)}$$

$$a = 0.45724\left(\frac{R^{2}T_{c}^{2}}{p_{c}}\right)$$

$$b = 0.07780\left(\frac{RT_{c}}{p_{c}}\right)$$

$$\alpha = [1 + \kappa(1 - T_{r}^{1/2})]^{2}$$

$$\kappa = 0.37464 + 1.5422\omega - 0.26992\omega^{2}$$

$$\omega = acentric factor$$

we have

$$\left(\frac{\partial H}{\partial T}\right)_{P} = T\left(\frac{\partial S}{\partial T}\right)_{P} + 0$$

Since at constant pressure dP = 0, and since

$$\begin{pmatrix} \frac{\partial H}{\partial T} \end{pmatrix}_{P} \equiv C_{P} \\ C_{P} = T \begin{pmatrix} \frac{\partial S}{\partial T} \end{pmatrix}_{P}$$

therefore,

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}C_P \tag{2.25}$$

So far, there are no restrictions on this equation.

**Step 4.** Now evaluate the second coefficient,  $(\partial S/\partial P)_T$ . From the relationship

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P$$

and the property of exactness described before, we have

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{2.26}$$

Step 5. The total differential, dS, is now complete as

$$dS = \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP$$
(2.27)

There are still no restrictions on this equation.

**Step 6.** Now evaluate  $(\partial V/\partial T)_P$  from an equation of state or numerically. If we choose PV = RT as the arbitrarily selected equation of state, then

$$V = RT/P$$
 and  $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$ 

and

$$\mathrm{d}S = C_P \frac{\mathrm{d}T}{T} - R \frac{\mathrm{d}P}{P}$$

We now have the total derivative of S as a function of properties only for any process. The integration to yield  $\Delta S$  is straightforward. This equation is now restricted to the ideal gas state, since that was the equation of state chosen to evaluate  $\partial V/\partial T_P$ .

This is a perfectly general method for any thermodynamic function:  $\Delta S$ ,  $\Delta H$ ,  $\Delta U$ ,  $\Delta G$ , etc. Since such equations contain only *properties of the system*, they are independent of path and can be tabulated for various fluids. Such tabulations form the basis for the various thermodynamic charts: T-S, H-S, etc.

*Example 2.2.* Calculate internal energy (U) and entropy (S) as a function of T and V.

It is sometimes more convenient to take T and V as independent variables rather than T and P. The method described above is perfectly general and can be applied here. Writing U and S as total differentials:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$
(2.28)

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$
(2.29)

Recall that

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{2.30}$$

Two relations follow immediately from differentiating Eq. (2.8):

$$\left(\frac{\partial U}{\partial T}\right)_{V} = T \left(\frac{\partial S}{\partial T}\right)_{V}$$
(2.31)

and

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial S}{\partial V}\right)_T - P \tag{2.32}$$

As a result of Eq. (2.30), Eq. (2.31) becomes

$$\left(\frac{\partial S}{\partial T}\right)_{V} = \frac{C_{V}}{T}$$
(2.33)

and as a result of Eq. (2.17), Eq. (2.32) becomes

$$\left(\frac{\partial U}{\partial V}\right)_{V} = T \left(\frac{\partial P}{\partial T}\right)_{V} - P \tag{2.34}$$

Combining Eqs. (2.28), (2.30), and (2.34) gives

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$
(2.35)

and combining Eqs. (2.29), (2.17), and (2.33) gives

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$
(2.36)

Equations (2.35) and (2.36) are general equations that express the internal energy and entropy of homogeneous fluids *at constant composition* as functions of temperature and molar volume. The coefficients of dT and dV are expressed in terms of measurable quantities.

#### 2.6.2. Useful Thermodynamic Relations

With these basic definitions and concepts we can now obtain a whole host of useful thermodynamic relations. Table 2.3 lists these relationships as functions of the process for both real systems and ideal gas systems. A distinction is also made, where necessary, between nonflow and flow systems, which are sometimes designated as closed and open systems, respectively.

# 2.7. Thermodynamic Analysis of Low-Temperature Systems

The fundamental tools for a low-temperature analysis are the first and second laws of thermodynamics. Assuming that the kinetic and potential energy terms in the first law can be neglected (frequently a valid assumption), the first law for a steady-state process such as a cryogenic refrigerator can be simplified to

$$\Delta H = Q - W_{\rm s} \tag{2.37}$$

where  $\Delta H$  is the summation of the enthalpy differences of all the fluids entering and leaving the system (or piece of equipment) being analyzed, Q is the summation of all heat exchanges between the system and its surroundings, and  $W_s$  is the net shaft work. There can be as many independent first law analyses as there are independent systems or pieces of equipment in the refrigeration and liquefaction systems. These can involve numerous unknowns, some of which may have to be fixed as parameters.

Process	W	Q	$\Delta U$	$\Delta H$
Isobaric (constant P)				
Real	$P(V_2 - V_1)$	$nC_P(T_2 - T_1)$	Q-W	$nC_P(T_2-T_1)$
Ideal gas	$nR(T_2 - T_1)$		$nC_V(T_2-T_1)$	
Isometric (constant $V$ )				
Real	0	$nC_V(T_2-T_1)$	Q	$\Delta U + \Delta (PV)$
Ideal gas			$nC_V(T_2 - T_1)$	$nC_P(T_2-T_1)$
Isothermal (constant $T$ )	$Q - \Delta U$	$\Delta U + W$	Q - W	$\Delta U + \Delta (PV)$
Real	$nRT\ln(V_2/V_1)$	$nRT\ln(P_1/P_2)$	0	0
Ideal gas	$nRT\ln(P_1/P_2)$	$nRT\ln(V_2/V_1)$		
Isentropic (constant S)				
Real (nonflow)	$-\Delta U$	0	-W	$\Delta U + \Delta (PV)$
Ideal gas (nonflow)	$(P_2V_2 - P_1V_1)/(1 - \gamma)$		$nC_V(T_2-T_1)$	$nC_P(T_2-T_1)$
	$nC_V(T_2-T_1)$			
Real (flow)	$-\Delta H$	0	$\Delta H - \Delta (PV)$	-W
Ideal (flow)	$\gamma (P_2 V_2 - P_1 V_1) / (1 - \gamma)$			
Polytropic				
Real (nonflow)	$Q - \Delta U$	$\Delta U + W$	Q-W	$\Delta U + \Delta (PV)$
	$(P_2V_2 - P_1V_1)/(1-n)$			
Ideal (nonflow)	$Q - nC_V(T_2 - T_1)$		$nC_V(T_2-T_1)$	$nC_P(T_2-T_1)$
Real (flow)	$Q - \Delta H$	$\Delta H + W$	$\Delta H - \Delta (PV)$	Q - W
Ideal (flow)	$n(P_2V_2 - P_1V_1)/(1-n)$			
Cyclic	$Q_{\rm net}$	W <sub>net</sub>	0	0

 Table 2.3
 Useful Thermodynamic Relationships

The choice of these parameters will generally be made on the basis of experience or convenience.

Application of the first law to the ideal work of isothermal compression in a refrigerator cycle with appropriate substitution for the heat summation reduces to

$$-W_{\rm s}/\dot{m} = T_1(S_1 - S_2) - (H_1 - H_2) \tag{2.38}$$

where  $\dot{m}$  is the mass rate of flow through the compressor, S is the specific entropy, H is the specific enthalpy, and the subscripts 1 and 2 refer to the inlet and exit streams, respectively, of the isothermal compressor. In a real system, an overall compressor efficiency factor will have to be incorporated in this equation to obtain meaningful results.

Evaluation of the refrigeration duty in a refrigerator cycle is dependent on the process chosen. For example, if the refrigeration process is isothermal, the refrigeration duty can be evaluated using the relation

$$Q = \dot{m}T(S_2 - S_1) \tag{2.39}$$

where T is the temperature at which the refrigeration takes place and the subscripts 1 and 2 refer to the inlet and exit streams of the process. On the other hand, if the refrigeration process involves only the vaporization of the saturated liquid refrigerant at constant pressure, evaluation of the duty reduces to

$$Q = \dot{m}h_{\rm fg} \tag{2.40}$$

where  $h_{\rm fg}$  is the specific heat of vaporization of the refrigerant. If the process is performed at constant pressure with the absorption of only sensible heat by the

refrigerant (e.g., warming a cold gas), the duty can be evaluated from

$$Q = \dot{m}(H_2 - H_1) \tag{2.41}$$

Similar first law balances could be written for other units of equipment used at low temperatures.

# 2.8. Joule–Thomson Coefficient

The slope at any point of an isenthalpic curve on a temperature–pressure diagram is called the Joule–Thomson (or J–T) coefficient. The J–T coefficient is usually denoted by  $\mu$  and is given by

$$\mu = \left(\frac{\partial T}{\partial P}\right)_{\!H}$$

The locus of all points at which the J–T coefficient is zero, i.e., the locus of the maxima of the isenthalpic curves, is known as the inversion curve and is shown as a dotted curve in Fig. 2.8. The region to the left and inside the inversion curve, where the J–T coefficient is positive, is the region of cooling; the region outside, where the J–T coefficient is negative, is the region of heating.

Hydrogen, helium, and neon have negative J–T coefficients at ambient temperature. Consequently, when used as refrigerants in a throttling process, they must be cooled either by a separate precoolant fluid or by a work-producing expansion to a temperature below which the J–T coefficient is positive. Only then will throttling cause a further cooling rather than heating.

Nitrogen, methane, and certain other fluids, on the other hand, have positive J–T co-efficients at ambient temperatures and hence produce cooling when expanded across a valve. Accordingly, any of these fluids can be used directly as the refrigerant in a throttling process without the necessity of a precooling step or expansion through a work-extracting device. Maximum inversion temperatures for some of the more common cyrogens are given in Table 2.4.



Figure 2.8 Joule–Thomson inversion curve.

	Maximum inversion temperature	
Fluid	K	°R
Oxygen	761	1370
Argon	722	1300
Nitrogen	622	1120
Air	603	1085
Neon	250	450
Hydrogen	202	364
Helium	40	72

 Table 2.4
 Maximum Inversion Temperature

*Example 2.3.* Show that the Joule–Thomson coefficient for a perfect gas is always zero.

The Joule-Thomson coefficient has been defined as

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \tag{2.42}$$

From calculus it can be shown that

$$\mu_{\rm J-T} = \left(\frac{\partial T}{\partial P}\right)_{\!H} = -\left(\frac{\partial T}{\partial H}\right)_{\!P} \left(\frac{\partial H}{\partial P}\right)_{\!T} \tag{2.43}$$

The expression  $(\partial H/\partial T)_P$  has previously been identified as the heat capacity,  $C_p$ . The expression  $(\partial H/\partial P)_T$  can be found by differentiating Eq. (2.9) and combining the result with Eq. (2.16) to yield

$$\left(\frac{\partial H}{\partial T}\right)_{P} = \left[V - T\left(\frac{\partial V}{\partial T}\right)_{P}\right]$$

The total differential for H,

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_P \mathrm{d}T + \left(\frac{\partial H}{\partial P}\right)_T \mathrm{d}P$$

becomes

$$dH = C_P dT + \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP$$
(2.44)

Setting dH = 0 (constant enthalpy), Eq. (2.45) gives the Joule–Thomson coefficient in terms of measurable thermodynamic properties as

$$\mu_{\rm J-T} = \frac{1}{C_P} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right]$$
(2.45)

For a perfect gas, V = RT/P, and

$$\left(\frac{\partial V}{\partial T}\right)_{P} = \frac{R}{P} = \frac{V}{T}$$

Therefore, for a perfect gas,

$$\mu_{\rm J-T} = \frac{1}{C_P} \left[ T\left(\frac{V}{T}\right) - V \right] = 0 \tag{2.46}$$

A perfect gas would not experience any temperature change upon expansion.

# 3. HEAT TRANSFER

All cryogenic systems operate, that is to say complete their required tasks, at very low temperatures. This fact requires a reasonably strong understanding of heat transfer and all associated technologies. As stated earlier, the best that one can hope for in some cases (e.g., cryogenic fluid storage) is to severely limit the energy transfer across boundaries. Since heat always flows from hot to cold and cannot be stopped, how it is controlled is the design aspect relating to heat transfer. In other cases (like gasification of cryogenic fluids) the ability to maximize the amount of heat introduced into the fluid is the desired design state. Due to the nature of the temperature difference between the everyday world we live in and the extremes of operating thermal conditions of cryogenic systems, a number of unique problems present themselves. These include, but not limited to: (1) variability of material properties, (2) thermal insulation, (3) fluid property differences for near-critical-point convection, (4) effects of thermal radiation, (5) equipment design characteristics and operation, (6) selection of instrumentation and control sensors, (7) transfer of cryogenic fluids, and (8) disposal and/or control of cryogenic boil-off. Each of these problems will be addressed in the remaining chapters of this book. Heat transfer at low temperatures is governed by the same three mechanisms present at ambient and elevated temperatures: conduction, convection, and radiation. It is not surprising, therefore, that all the general equations are appropriate for low-temperature applications as long as they are adjusted for the property changes in both materials and fluids.

# 3.1 Conductive Heat Transfer

Another method of determining the heat transfer rate is in the expression:

$$Q = S(K_H - K_C)$$

where  $K_H$  and  $K_C$  are the thermal conductivity integrals at the evaluated temperature  $T_H$  and  $T_C$ , respectively. These two terms are defined as:

$$K_H = \int_0^{T_H} (k_t \mathrm{d}t) \text{ and } K_C = \int_0^{T_C} (k_t \mathrm{d}T)$$

and S is defined as a conduction shape factor as

$$1/S = \int_{x_1}^{x_2} (\mathrm{d}x/A(x))$$

where  $k_t$  is the material thermal conductivity at some temperature within the temperature field expressed by the integral; dx is the change in length along the axis of heat transfer; and A is the cross-sectional area of heat transfer.

The quantities  $K_H$  and  $K_C$  represent the integrated thermal conductivity for any solid material that has had its thermal conductivity variation with temperature determined. The values of  $K_H$  and  $K_C$  are also useful when their difference is divided by the difference of  $T_H$  and  $T_C$  and becomes the apparent thermal conductivity of the material, expressed as

$$K_M = (K_H - K_C)/(T_H - T_C)$$

Figures 2.9 and 2.10 are graphical depictions of thermal conductivity integrals for some metals and insulators, respectively.

The conduction shape factor S is derived from the Fourier equation and simply places all the physical parameters of the shape of the material into a single integral. This allows for various geometric shapes to be evaluated and conduction shape factors to be determined based on the desired physical dimension of interest, such as wall thickness or sphere diameters. Table 2.5 gives some representative conduction shape factors for various geometries of interest. These geometries are pictured in Fig. 2.11.

With this simple expression it is possible to get a good engineering estimate on the heat balance around various cryogenic components under steady-state conditions

$$Q = -kA\frac{\mathrm{d}T}{\mathrm{d}x}\tag{2.47}$$

where Q is the heat transferred, k the material thermal conductivity (normally a function of temperature), A the area of the material through which the heat is transferred and dT/dx the change in temperature observed in the material in the x direction due to the heat transfer.

If Q, k, and A are constant, the relation becomes

$$Q = -kA\frac{T_2 - T_1}{\Delta_x} \tag{2.48}$$

This relation is useful when determining the heat transfer through a layer of insulation or a series of insulation materials. If the conduction is through insulation wrapped around a pipe, the relationship is modified to

$$Q = -kA\frac{\mathrm{d}T}{\mathrm{d}r} = 2 \ \pi \ Lk\frac{T_1 - T_2}{\ln(r_2/r_1)}$$
(2.49)

where L is the length of the pipe,  $r_1$ ,  $r_2$  the inside and outside radii of the insulation and  $T_1$ ,  $T_2$  the corresponding temperatures at these locations.

For nonsteady-state conductive heat transfer, a heat balance may be made around a volume element of material of dimensions dx, dy, and dz. In the x direction, the heat transferred into the volume element is given by

$$\mathrm{d}Q_x = -k\,\mathrm{d}y\,\mathrm{d}z\frac{\partial T}{\partial x}\tag{2.50}$$

The heat leaving the volume element is

$$\mathrm{d}Q'_x = \mathrm{d}Q_x + \frac{\partial \mathrm{d}Q_x}{\partial x}\,\mathrm{d}x\tag{2.51}$$

If k is constant, then



Figure 2.9 Thermal conductivity integrals of metals. Data provided from S. Courts, Lakeshore Cryotronics.

$$dQ'_{x} - dQ_{x} = k \, dy \, dz \, dx \frac{\partial^{2} T}{\partial x^{2}}$$
(2.52)

Similar expressions are valid for the other two directions. If heat is stored in the volume element, then


**Figure 2.10** Thermal conductivity integrals of insulating materials. Data provided from S. Courts, Lakeshore Cryotronics.

$$\mathrm{d}Q_s = \mathrm{d}Q_x - \mathrm{d}Q'_x + \mathrm{d}Q_y + \mathrm{d}Q_z - \mathrm{d}Q'_z \tag{2.53}$$

but

$$\mathrm{d}Q_s = C_P \rho \,\mathrm{d}x \,\mathrm{d}y \,\mathrm{d}z \frac{\partial T}{\partial \theta} \tag{2.54}$$

 Table 2.5
 Example Conduction Shape Factors<sup>a</sup>

Geometry	Shape factor
[1] Plane wall or slab	$S = A/\Delta x$
[2] Hollow cylinder	$S = \frac{2\pi L}{\ln(D_0/D_1)}$
[3] Hollow sphere	$S=rac{2\pi D_0 D_i}{(D_0-D_i)}$
[4] Isothermal cylinder placed vertically in a semi-infinite medium	$S = \frac{2\pi L}{\ln(4L/D)}$
[5] Isothermal cylinder buried in a semi-infinite medium	$S = \frac{2\pi L}{\cosh^{-1}(2H/D)}$
[6] Isothermal sphere buried in a semi-infinite medium	$S=\frac{8\pi D}{1-(D/4H)}$
[7] Cylinder centered in a large plate	$S = \frac{2\pi L}{\ln(4H/D)}$

 $^{\mathrm{a}}$  See Fig. 2.11 for correlated sketch of referenced geometry.

so

$$\left(\frac{\partial T}{\partial \theta}\right) = \alpha \left[ \left(\frac{\partial^2 T}{\partial x^2}\right) + \left(\frac{\partial^2 T}{\partial y^2}\right) + \left(\frac{\partial^2 T}{\partial z^2}\right) \right]$$
(2.55)

where  $\theta$  is the time,  $C_P$  and  $\rho$  are the heat capacity and density of the material,



Figure 2.11 Sketch of geometries referred to in Table 2.5.

respectively, and  $\alpha$  is defined as  $k/\rho C_P$ . At a steady state,  $\partial T/\partial \theta = 0$ . The solution of Eq. (2.55) involves either the separation of variables or the use of integral transforms (usually Laplace transforms). For regular geometries, plots have been developed that permit rapid and reasonably reliable solutions even at low temperatures for heating or cooling times.

## 3.2. Convective Heat Transfer

Thermal convection is the transfer of heat from a fluid to a colder surface by means of fluid particle motion. There are two types of *convective heat transfer*. Forced convection occurs when a fluid is forced or pumped past a surface; *free convection* or natural convection occurs when fluid motion is caused by density differences within the fluid. In either case, the basic equation is

$$Q = h_{\rm c}A(T_{\rm s} - T_{\rm b}) \tag{2.56}$$

where  $h_c$  is the individual heat transfer coefficient,  $T_s$  is the surface temperature, and  $T_b$  is the bulk fluid temperature. The individual heat transfer coefficient is critical in the solution of Eq. (2.56) and must generally be obtained with the aid of some empirical relationship that has been found to correlate the convective heat transfer reasonably well for a specific geometry or flow pattern. The empirical relationships used to obtain the individual heat transfer coefficients at low temperatures are very similar to the relationships used at ambient temperatures.

Tables 2.6–2.8 provide some useful heat transfer relationships for low-temperature heat exchangers for a variety of operating conditions. The units for the relationships in these tables are in consistent American engineering units. Conversion factors to other systems of measurement are found in the Appendix.

If heat is transferred from one fluid to another separated by a pipe as in a heat exchanger, then Eq. (2.56) can be modified to include the individual heat transfer coefficients for both fluids in an overall heat transfer coefficient as

$$Q = U_{\rm o} A_{\rm o} \Delta T_{\rm overall} \tag{2.57}$$

where  $U_0$  is based on the outside surface area  $A_0$ . If the inside surface area is used, the relationship can be modified to

$$Q = U_{\rm i} A_{\rm i} \Delta T_{\rm overall} \tag{2.58}$$

If the heat exchange is across a pipe,  $U_i$  can be obtained from

$$U_{\rm i} = \frac{1}{1/h_{\rm i} + \Delta r_{\rm p}A_{\rm i}/k_{\rm p}A_{\rm p,lm} + A_{\rm i}/h_{\rm o}A_{\rm o}}$$
(2.59)

where  $h_i$  is the inside heat transfer coefficient,  $\Delta r_p$  is the thickness of the pipe,  $A_i$  is the inside surface area,  $k_p$  is the thermal conductivity of the pipe,  $A_{p,lm}$  is the log mean area of the pipe given by  $(A_o - A_i)[\ln (A_o/A_i)]$ ,  $A_o$  is the outside surface area, and  $h_o$  is the outside heat transfer coefficient. A similar expression can be written for  $U_o$ . For a flat wall, Eq. (2.59) reduces to

$$U_{\rm i} = U_{\rm o} = \frac{1}{1/h_{\rm i} + \Delta x/k + 1/h_{\rm o}}$$
(2.60)

Table 2.6 Empirical H	eat Transfer and Corresponding	g Pressure Drop Relationships for Concentric Tube and Extended Sur	urface Heat Exchangers
Type	Flow conditions	Empirical heat transfer equation	Empirical pressure drop/length equation
Straight tubular pipe	Flow inside, Re < 2100; no phase change (gas)	$h = \left[ 3.658 + \frac{0.0668(D_e/L)\text{Re}\text{Pr}}{1 + 0.04(D_e/L)\text{Re}\text{Pr}^{2/3}} \right] \frac{k}{D_e} \frac{\Delta P}{\Delta L} = \frac{\Delta P}{\Delta L}$	$\vec{c} = \frac{32 G^2}{\text{Re} g_c D_e \rho}$
Straight tubular pipe	Flow inside, 2100 < Re < 10,000; no	$h = 2.439 \times 10^{-6} (\mathrm{Re}^{2/3} \times 125) \left[ 1 + \left(\frac{D_{\mathrm{e}}}{\mathrm{L}}\right)^{2/3} \right] \left(\frac{C_{\mathrm{P}}}{\mathrm{D}_{\mathrm{e}}}\right) \left(\frac{\mu_{\mathrm{f}}}{\mu_{\mathrm{b}}}\right)^{-0.14} \frac{\Delta P}{\Delta L}^{\frac{1}{2}}$	$\frac{P}{C} = \frac{0.158 \ G^2}{\text{Re}^{0.2} \ g_c D_e  ho}$
Straight tubular pipe	phase change (gas) Flow inside, $Re > 10,000$ ; no phase change (gas)	$h = 0.023 \ C_P G \mathrm{Re}^{-0.2} \ \mathrm{Pr}^{-2/3} \qquad \qquad$	$\frac{\mathbf{p}}{C} = \frac{0.092 \ G^2}{\mathrm{Re}^{0.2} \ g_{\mathrm{c}} D_{\mathrm{e}} \rho}$
Helical tubular pipe	Flow inside, Re > 10,000; no phase change (gas)	$h = 0.023 \ C_P G \text{Re}^{-0.2} \ \text{Pr}^{-2/3} [1 + 3.5 (D_e/D_h)] \qquad \frac{\Delta P}{\Delta L}^{-2}$	$\frac{1}{C} = rac{0.092 \ G^2 [1 + 3.5 (D_{\rm e}/D_{\rm h})]}{{ m Re}^{0.2} \ g_{\rm c} D_{\rm e}  ho}$
Collins tubing	Flow in annulus, 400 < Re < 10,000; no phase change (gas)	$h = 0.118 \ C_P G \mathrm{Re}^{-0.2} \mathrm{Pr}^{-2/3}$ $\frac{\Delta P}{\Delta L} = \frac{\Delta P}{\Delta L}$	$C = \frac{0.952 G_{\text{max}}^2}{\text{Re}^{0.2} g_{\text{c}} D_e \rho}$
For tubular pipe: $D_e = insid$ or wetted tube surface area: For Collins tubing: $D_e = 4(i)$ Evaluate fluid properties for these equations are for use	e pipe diameter; for noncircular tub for annulus, $D_e = D_2 - D_1$ , where $J'_a/A_w$ ), where $V_a = \operatorname{active}$ flow volu all relations at the mean film tempe with 51 units.	es, $D_c = 4(A_cL/A_w)$ , where $A_c =$ inside free-flow cross-sectional area, $L =$ length ( $D_2 =$ inside diameter of outer pipe and $D_1 =$ outside diameter of inner pipe; $D_h =$ me in annulus, $A_w =$ wetted area in annulus, including fins. srature, $T_m = 0.5(T_w + T_b)$ , where $T_w =$ tube wall temperature and $T_b =$ bulk tem	h of pipe, and $A_w$ = heat transfer $D_h$ = diameter of helix. Emperature of fluid. Constants in

Table 2.7 Empirical Heat T         Heat Exchangers	ransfer and Corresponding Pressure Dr	p Relationships for Flows Norm	al to Outside of Tubes on Shell Side of Coiled Tube
Type	Flow conditions	Empirical heat transfer equation	Empirical pressure drop/tube equation
Banks of staggered tubes	Flow normal to outside of tubes. $2000 < \text{Re} < 3.2 \times 10^4$ :	$h = 0.33 \ C_P G  \mathrm{Re}^{-0.4} \ \mathrm{Pr}^{-2/3}$	$\frac{\Delta P}{\Delta N} = \left[ 0.5 + 0.235 (X_{\rm T} - 1)^{-1.08} \right] {\rm Re}^{-0.15}  G_{\rm max}^2 / g_{\rm c} \rho$
Banks of in-line tubes	no phase change (gas) Flow normal to outside of tubes, $2000 < \text{Re} < 3.2 \times 10^4$ ;	$h = 0.26 \ C_P G \mathrm{Re}^{-0.4} \mathrm{Pr}^{-2/3}$	$\frac{\Delta P}{\Delta N} = [0.088 + 0.16 X_{\rm L} (X_{\rm T} - 1)^{-n}] {\rm Re}^{-0.15}  G_{\rm max}^2 / g_{\rm c} \rho$
	no phase change (gas)		
$\operatorname{Re} = D_{\circ}G_{\operatorname{max}}/u$ where $D_{\circ} = \operatorname{outs}$	ide diameter of tubes: $G_{\text{min}} \equiv \dot{m}/A_{\text{min}}$ with A	= minimum open free-flow area b	etween tubes: $X_{\tau} \equiv$ transverse nitch/tube outside diameter:

le of Coiled Tube	
Tubes on Shell Sic	
ormal to Outside of	
ships for Flows Nc	
tre Drop Relations	
orresponding Pressu	
at Transfer and Co	
7 Empirical He	changers
able 2.	eat Ex

 $\frac{\text{Re} = D_0 G_{\text{max}}/\mu, \text{ where } D_0 = \text{outside diameter of tubes; } G_{\text{max}} = \dot{m}/A_{\text{min}}, \text{ with } A_{\text{min}} = \text{minimum open free-flow area between tubes; } A_T = \text{transverse puon/unce output}, N = \text{total number of tubes in line of flow; } X_L = \text{longitudinal pitch/tube outside diameter; } n = 0.43 + (1.13/X_L). Fluid properties for all relations are evaluated at the mean film temperature, <math>T_m = 0.5(T_w + T_b)$ , where  $T_w = \text{tube wall temperature and } T_b = \text{bulk temperature of fluid.}$ 

Table 2.8	Empirical Heat T	ransfer and C	Corresponding	Pressure	Drop	Correlations	for
Brazed Alu	minum Plate-Fin I	Heat Exchang	gers <sup>a</sup>				

Type and flow conditions	Empirical heat transfer equation	Empirical pressure drop/length equation
Straight fins, $500 < \text{Re} < 10^4$ ;	$h = 0.0291 \mathrm{Re}^{-0.24}$ $\mathrm{Pr}^{-2/3} C_P G$	$\frac{\Delta P}{\Delta L} = \frac{(0.0099 + 40.8 \mathrm{Re}^{-1.033})G^2}{g_{\mathrm{c}}\rho D_{\mathrm{c}}}$
h = 7.87  mm (0.310  in.); w = 0.15  mm (0.006  in.); 492  fins/m (12.5  fins/in.);	·	
no phase change (gas) Wavy fins, $300 < \text{Re} < 10^4$ ;	$h = 0.085 \mathrm{Re}^{-0.265}$ $\mathrm{Pr}^{-2/3} C_P G$	$\frac{\Delta P}{\Delta L} = \frac{(0.0834 + 23.6 \mathrm{Re}^{-0.062})G^2}{g_{\mathrm{c}}\rho D_{\mathrm{e}}}$
h = 9.53  mm (0.375  in.); w = 0.20  mm (0.008  in.); 591  fins/m (15  fins/in.); $r_{2}$ phase change (gap)		
Herringbone fins, $400 < \text{Re} < 10^4$ ; h = 10.82  mm (0.426  in.); w = 0.15  mm (0.006  in.); 472  fins/m (12  fins/in.); no phase change (gas)	$h = 0.555(\text{Re} + 500)^{-0.482}$ $\text{Pr}^{-2/3} C_P G$	$\frac{\Delta P}{\Delta L} = \frac{7.04G^2 \operatorname{Re}^{-0.547}}{g_{\rm c}\rho D_{\rm e}}$

<sup>a</sup> To match present vendor specifications, dimensions are also given in customary English units.  $D_e = 4(A_cL/A_w)$ , where  $A_c =$  inside free-flow cross-sectional area, L = length of pipe, and  $A_w =$  heat transfer or wetted tube surface area. Evaluate fluid properties for all relations at mean film temperature,  $T_m = 0.5(T_w + T_b)$ , where  $T_w =$  tube wall temperature and  $T_b =$  bulk temperature of fluid.

Heat transfer from a condensing vapor to a cooler surface may be considered as a special case of convective heat transfer. Heat transfer calculations with condensing vapors are generally made using a relation similar to Eq. (2.56), where  $T_{\rm b}$  is the temperature of the condensing vapor and  $T_{\rm s}$  is the temperature of the surface upon which condensation occurs. For filmwise condensation on the outside of horizontal tubes, the convective heat transfer co-efficient can be obtained from

$$h_{\rm c} = 0.725 \left[ \frac{k^3 \rho^2 g h_{\rm fg}}{\mu_{\rm f} D_{\rm o} N \Delta T} \right]^{1/4} \tag{2.61}$$

where  $h_{\rm fg}$  is the latent heat of vaporization, N is the number of rows of tubes in the vertical plane,  $D_{\rm o}$  is the outside diameter of the tubes, and  $\Delta T$  is the temperature difference between the saturated vapor and the outside tube surface. For filmwise condensation on the outside of vertical tubes, the convective heat transfer coefficient relationship is modified to

$$h_{\rm c} = 0.942 \left[ \frac{k^3 \rho^2 g h_{\rm fg}}{\mu_{\rm f} L \Delta T} \right]^{1/4} \tag{2.62}$$

Heat transfer from a surface to a boiling liquid can also be considered a special case of convective heat transfer. There are commonly seen two types of boiling: nucleate and film boiling. Within the nucleate boiling category, there are two distinct classifications: natural convection (also known as pool boiling) or forced convection



**Figure 2.12** Pooling boiling depictions: (a) saturated conditions generate vapor and raises the bulk fluid temperature while (b) subcooled conditions shown allows for no vapor generation but does raise in the bulk fluid temperature, as well.

boiling. There is a further subdivision of two primary boiling types (nucleate and film) based upon whether the boiling fluid is under saturated or sub-cooled conditions. The nucleate boiling conditions are depicted in Fig. 2.12 and 2.13, while 2.14 illustrates the filming boiling process. Most experimental work at low temperatures has been conducted on pool boiling. Such studies have shown that the boiling action at these temperatures is also largely dependent on the temperature difference between the submerged surface and the boiling liquid. Unfortunately, the available information on boiling liquids at low temperatures is limited and also shows wide scatter in the experimental data. Figure 2.15 shows typical experimental nucleate and film pool boiling data for nitrogen at 1atm compared with predictive correlations. Figures 2.16–2.18 give similar data for oxygen, hydrogen, and helium. See "Suggested Reading" at the end of the book for the original data sources called out on Figs. 2.15–2.18.

#### 3.3. Radiative Heat Transfer

Thermal radiation involves the transfer of heat from one body to another at a lower temperature by electromagnetic waves passing through the intervening medium. Radiant energy striking a material may be partly absorbed, transmitted, or reflected.



**Figure 2.13** Forced convection boiling: (a) subcooled conditions again allow for no vapor generation while (b) saturated or bulk boiling generates vapor and any number of different vapor-liquid flow conditions.



**Figure 2.14** Film boiling occurs when a vapor covers the super-heated bottom surface: (a) if conditions are subcooled, then no vapor will be generated, and (b) at saturated conditions large amounts of vapor can be formed.

For some materials, for example glass or plastic, this can be written as

$$\alpha + \tau + \rho = 1 \tag{2.63}$$

where  $\alpha$  is the absorptivity,  $\tau$  is the transmissivity, and  $\rho$  is the reflectivity. For an opaque material,  $\alpha + \rho = 1$ , and for a blackbody,  $\alpha = 1$ . The emissive power *E* of a unit surface is the amount of heat radiated by the surface per unit of time. The



Figure 2.15 Experimental and predictive nucleate and film boiling of nitrogen at 1 atm.



Figure 2.16 Experimental and predictive nucleate and film boiling of oxygen at 1 atm.

emissivity  $\epsilon$  of a surface is defined by

$$\epsilon = E/E_{\rm b} \tag{2.64}$$

where  $E_{b}$  is the emissive power of a blackbody at the same temperature. The emissive power for a blackbody is given by

$$E_{\rm b} = \sigma T^4 \tag{2.65}$$



Figure 2.17 Experimental and predictive nucleate and film boiling of hydrogen at 1 atm.



Figure 2.18 Experimental and predictive nucleate and film boiling of helium at 1 atm.

where  $\sigma$  is the Stefan–Boltzmann constant. For a real surface, the relation is modified to

$$E = \epsilon \sigma T^4 \tag{2.66}$$

When two bodies within visual range of each other are separated by a medium that does not absorb radiation, an energy exchange occurs as a result of reciprocal processes of emission and absorption. The net rate of heat transfer from one surface at  $T_1$  to another surface at  $T_2$  can be calculated from

$$Q = \sigma A_1 F_{\rm A} F_{\rm E} (T_1^4 - T_2^4) \tag{2.67}$$

where  $A_1$  is the surface area of one of the bodies,  $F_A$  is a shape and orientation factor for the two bodies relative to area  $A_1$ , and  $F_E$  is the emission and absorptance factor for the two bodies. If the surface of one body is small or enclosed by the surface of the other body,  $F_A = 1$ ; otherwise,  $F_A$  must be evaluated. For a surface  $A_1$  radiating to a large area or space,  $F_E = \epsilon_1$ . For two large parallel plates with a small space between them,

$$F_{\rm E} = \frac{1}{1/\epsilon_1 + 1/\epsilon_2 - 1} \tag{2.68}$$

For a sphere of radius  $r_1$  inside another sphere of radius  $r_2$ ,

$$F_{\rm E} = \frac{1}{1/\epsilon_1 + (r_1/r_2)^2 [(1/\epsilon_2) - 1]}$$
(2.69)

For a long cylinder of radius  $r_1$  inside another cylinder of radius  $r_2$ ,

$$F_{\rm E} = \frac{1}{1/\epsilon_1 + (r_1/r_2)[(1/\epsilon_2) - 1]}$$
(2.70)

For the case where  $F_A = 1$  and  $F_E = \epsilon_1$ , we can define a radiative heat transfer coefficient as

$$h_{\rm r} = \frac{\sigma}{T_1} \left( \frac{T_1^4 - T_2^4}{T_1 - T_2} \right) \tag{2.71}$$

This can then be used to determine the heat transferred by radiation from the relation

$$Q = h_{\rm r} A_1 (T_1 - T_2) \tag{2.72}$$

# 4. MOMENTUM TRANSFER

Cryogenic fluids are often handled near their boiling point. Thus, flow is usually complicated because vaporization occurs, resulting in two-phase flow. The transition from liquid to vapor depends on the heat influx and pressure changes encountered in the system.

For single-phase flow, the most important point to recognize is the distinction between laminar and turbulent flow. For low temperatures, the same concepts that have been developed for ambient flow apply. For flows with Reynolds numbers less than 2100, laminar flow is assumed to occur; and for flows with Reynolds numbers greater than 3000, turbulent flow is assumed to occur. The range in between 2100 and 3000 is normally considered the transition region between laminar and turbulent flow. Thus, the empirical relationships that have been used successfully in calculating, for example, the pressure drop in a pipe at ambient conditions are also valid for systems using cryogenic fluids.

Tables 2.5–2.7 provide some useful relationships to determine the empirical heat transfer coefficient and pressure drop per unit length of many common heat exchangers.

In cryogenic systems, two-phase flow cannot be avoided, particularly during the cooldown of transfer lines. If a cooldown situation is encountered frequently, complete system performance reliability requires design for this condition. It takes only a slight localized heat influx or pressure drop to cause the evaporation of part of the fluid. Vapor in such lines can significantly reduce the liquid transfer capacity. This transition from liquid to vapor is usually an unequilibrated condition and presents an undefined problem for design purposes.

The Martinelli–Nelson correlation has been found to be useful for estimating pressure drop for a single-phase stream under steady-state flow conditions. However, this correlation, developed for ambient conditions, has a tendency to underestimate the pressure drop by as much as 10–30% because of the high tendency of cryogenic fluids to vaporize.

Another fluid problem encountered rather frequently is that of *cavitation* in pumps. Cavitation begins at a pressure slightly below where vaporization just begins. The difference in pressure between cavitation and normal vaporization is equal to the net positive suction head minus the drop in head pressure in the pump. Normally, this must be determined experimentally and is a characteristic of the pump and the fluid.

A critical flow can be achieved in the transfer of a cryogenic fluid. In such a situation, the flow rate of the fluid cannot be altered by lowering the downstream

pressure as long as the supply pressure remains constant. Such a situation is due to the increased down-stream vaporization, which reduces the cross-sectional area available for liquid transfer.

Cooldown of cryogenic systems involves a period of surging flow and pressure fluctuations with accompanying sound effects. The primary factors that affect surging and maximum pressure include inlet pressure and temperature, pipe length and diameter, pipe precooling, throttling, and liquid properties. Other factors such as heat capacity, external heat leak, and pipe wall thickness have a minor effect on surging, because the pipe temperature undergoes little change during such a surge.

# 5. HEAT LEAK AND PRESSURE DROP IN CRYOGENIC TRANSFER LINES

Cryogenic fluid transfer presents a number of challenges to any designer but two problem areas, in particular, have wide ranging impacts on the overall system design: (1) heat leak in cryogenic transfer, and (2) pressure drop during cryogenic transfer of fluids.

The transfer piping design should accommodate the desired heat transfer requirements as well as the fluid transfer conditions necessary to accommodate the overall system design. A comparison of the heat leak into a bare pipe vs. those with various insulations techniques is given in Table 2.9 for liquid nitrogen. The effect of improved insulation techniques, such as vacuum jacketed pipe (VJP), is obvious and can result in reduced heat loads of several orders of magnitude over bare pipes. VJP comes in rigid and flexible configurations to accommodate the designer's need for making bends, etc. The flexible configuration requires a more complex and slightly less efficient insulation scheme and therefore do not offer the same performance as the rigid versions but is still very good vs. the nonvacuum jacketed alternatives. Both rigid and flexible transfer lines come in various sizes and a number of commercial vendors are available to supply these types of units.

Table 2.10 gives estimated heat leak for liquid nitrogen, oxygen, and hydrogen with various line sizes. An additional consideration of VJP is the required cooldown heat removal necessary to allow the line to efficiently transfer cryogenic fluids. Note that flow is not a parameter. This is the case because fully developed turbulent flow is assumed. For laminar flow to exist, the pipe diameter would have to be extremely large, resulting in excessive costs and unnecessarily high heat leak into the system. At turbulent flow conditions, the controlling insulating parameter to heat leak into the fluid is the vacuum jacket around the transfer pipe. Solid thermal conductivity through the pipe walls, as well as the heat transfer coefficient to turbulent cryogenic

**Table 2.9** Comparison of Insulation Techniques for FluidTransfer Piping Versus Bare or Non-insulated Piping IllustratesNeeds for Insulation (Courtesy Technifab Products, Inc.)

Pipe comparison Heat leak Btu/ft/hr	
Bare copper pipe	200.0
Foam insulated pipe	20.0
Bare vacuum pipe	4.0
Vacuum jacketed pipe from TPI	0.47

Vacuum jacketed p	piping heat le	eak in Btu/h	r/ft and (Wa	utts/ft)		
	L	N <sub>2</sub>	L	O <sub>2</sub>	L	H <sub>2</sub>
Line Size	Rigid	Flex	Rigid	Flex	Rigid	Flex
$\frac{3}{4}$ OD × 1 $\frac{1}{4}$ NPS	0.37 (0.11)	0.97 (0.28)	0.37 (0.11)	0.96 (0.28)	0.40 (0.12)	1.05 (0. 31)
$\frac{3}{4}$ " NPS $\times 2$ " NPS	0.43 (0.13)	1.21 (0.25)	0.42 (0.12)	1.19 (0.35)	0.46 (0.13)	1.29 (0.38)
1" NPS $\times 2\frac{1}{2}$ " NPS	0.47 (0.14)	1.43 (0.42)	0.47 (0.14)	1.41 (0.41)	0.51 (0.15)	1.54 (0.45)
$1\frac{1}{2}$ " NPS $\times \tilde{3}$ " NPS	0.58 (0.17)	1.74 (0.51)	0.57 (0.17)	1.71 (0.50)	0.63 (0.18)	1.89 (0.55)
$2^{\ddagger}$ NPS $\times$ 4" NPS	0.79 (0.23)	2.37 (0.70)	0.65 (0.19)	1.95 (0.57)	0.85 (0.25)	2.56 (0.75)
3" NPS × 5" NPS	0.98 (0.29)	2.95 (0.86)	0.84 (0.25)	2.52 (0.74)	1.08 (0.32)	3.24 (0.95)
4" NPS × 6" NPS	1.28 (0.38)	3.85 (1.13)	1.01 (0.30)	3.03 (0.89)	1.40 (0.41)	4.22 (1.24)
6" NPS × 8" NPS	1.65 (0.48)	4.97 (.146)	1.36 (0.40)	4.10 (1.20)	1.83 (0.54)	5.50 (1.61)

**Table 2.10**Estimate Heat Leak for Vacuum Jacketed Piping, Both Rigid and Flexible.(Courtesy of PHPK Technologies, Inc.)

flow are both negligible to that of the radiation heat load through the vacuum space per length of pipe. This radiation heat load is a first order effect relating to surface areas, the larger the surface area, the larger the heat load. The internal and external surface areas of pipes are driven by their respective diameters.

Table 2.10 also shows very little increase in heat leak in changing the fluid transferred. All three fluids have heat leak conditions within about 10% of each other even though the temperature changed from 90 to 20 K. From simple radiation heat transfer calculations alone, one might expect a heat leak increase by a factor of over 400 (= $(90/20)^4$ ). However, the actual case is that the hydrogen temperatures do a much better job of cryopumping than do oxygen or nitrogen cooled surfaces. Thus at 90 K, there is still some small residual gas conduction, which is not present at 20 K.

Table 2.11 illustrates using vacuum jacket valves the cooldown loss in Btu for various sizes at two temperatures, liquid nitrogen and liquid hydrogen, and then compares the cooldown loss to the steady-state heat leaks of these units. The heat leak into vacuum jacketed (VJ) valves is expected to be higher due to the (1) increase of the penetrations into the VJ around the valve body, (2) the required increased

	Cool-down and	heat leak perform	mance information (jack	teted)
	Cool-dow	n loss Btu	Steady state heat	t leak Btu/hr (W)
Valve Size	80 K	20 K	80 K	20 K
$\frac{1}{2}$ "	81	86	10.5 (3.1)	11.6 (3.4)
$\frac{3}{4}$ "	81	86	10.5 (3.1)	11.6 (3.4)
1"	99	105	10.5 (3.1)	11.6 (3.4)
$1\frac{1}{2}$ "	189	200	13.7 (4.0)	15.0 (4.4)
2"	324	342	18.1 (5.3)	20.0 (5s.9)
3"	990	1045	39.7 (11.6)	44.1 (12.9)
4"	1260	1330	47.9 (14.0)	53.1 (15.6)

**Table 2.11**Estimated Performance Data for Different Size Vacuum Jacketed Valves.(Courtesy of PHPK Technologies, Inc.

support for the internal valve components, (3) heat from the power source to drive the valve, (4) instrumentation required to operate and monitor the valve, etc. Additional heat leak considerations should be included for the mechanical connections between VJP segments and the components included in the fluid systems. Each individual connection can be roughly estimated to be about 1.24 times a one-foot segment of the same size line.

The second design problem is pressure drop in cryogenic transfer lines. Two figures (Figs. 2.19 and 2.20) are provided to show the expected pressure drop per foot of pipe vs. flow in gallons per minute for nitrogen and hydrogen. Inside pipe diameter is the parameter for the data lines. Additionally, Fig. 2.21 is provided and illustrates the pressure drop differences of rigid pipe vs. flexible pipe for flowing liquid nitrogen. The increase in pressure drop can be directly attributed to the internal design use of welded bellows to form the interior pipe walls. This is true in all, not just cryogenic, fluid transfer involving flexible lines.

The values shown in Table 2.10 and the graphs of Figs. 2.19 and 2.20 can be expected from currently available, commercially fabricated transfer lines using current vacuum-jacketing technology. These values have been confirmed by the two largest US manufacturers of this equipment. At their request, no credit is given, as they have no control over how the data will be used and accordingly wish to assume no responsibility for potential misuse by others.



Flow rate of Liquid Nitrogen (GPM)

Figure 2.19 Pressure drop of liquid nitrogen in Schedule 5 rigid pipe.



Flow rate of Liquid Hydrogen (GPM)

Figure 2.20 Pressure drop of liquid hydrogen in Schedule 5 rigid pipe.

*Example 2.4.* Given the following data, calculate the heat leak and pressure drop for liquid hydrogen in a commercially available vacuum-insulated transfer line:

Liquid hydrogen transfer rate: 250 gpm Maximum allowable heat leak: 800 Btu/hr Acceptable pressure drop: 20–30 psi Desirable pipe size: 2 in. i.d.

**Heat leak**. Table 2.10 shows that a 2 in. pipe will have a heat leak of 0.85 Btu/hr per foot of pipe in which liquid hydrogen is flowing. The various fittings (spacers, valves, bayonet connectors, etc.) will each amount to 1.24 equivalent feet of pipe.

Therefore, if 800 Btu/hr can be accommodated, the maximum run of equivalent pipe is 800/0.85 = 941 ft of pipe. If there were 24 components (a large number), their equivalent length would be  $24 \times 1.24 = 41$  ft. Thus, the pipe run could comprise 900 ft of pipe and 24 components.

**Pressure drop.** Figure 2.20 for hydrogen flow shows a pressure drop of 0.034 psi per foot of 2 in. pipe.

If the tolerated pressure drop is 20 psi, then the maximum length of pipe is 20/0.034 = 588 ft of pipe.

If the acceptable pressure drop is 30 psi, then the maximum length of pipe is 30/0.034 = 882 ft of pipe.

				Tube/Si	chequie 5	mpe - psi	roont	Flex Hose	a • psi/10f				
Flow	3/4"	3/4	inch	1 ir	nch	1 1/2	inch	2 in	nch	3 in	ch	4 in	ch
gpm)	Tube	Pipe	Flex	Pipe	Flex	Pipe	Flex	Pipe	Flex	Pipe	Flex	Pipe	Flex
0.4	0.052	-	1.									-	1.2.4.3
0.6	0.109		0.033					1.000					
0.8	0.185	0.033	0.058						1.0		1.		
1	0.281	0.050	0.091			1.00							
2	1.047	0.182	0.363	0.051	0.082								1.1.1
3	2.291	0.392	0.816	0.109	0.184		-						
4	4.009	0.681	1.451	0.188	0.326		0.040				1.00		
5	6.202	1.046	2.267	0.287	0.510	0.038	0.062		10.100				
6	8.868	1.490	3.264	0.407	0.734	0.054	0.089						
8	15.622	2.608	5.803	0.708	1.305	0.092	0.159	-	0.035		1.14		
10		4.035	9.067	1.091	2.040	0.141	0.248	0.043	0.055		1.		
15		8.95		2.406	4.589	0.306	0.558	0.092	0.124	2	1.1.4	-	
20	4	15.79		4.231	8.159	0.534	0.991	0.159	0.221				
25				6.56	12.748	0.824	1.549	0.244	0.346	0.033	0.041	-	
30				9,40	18.358	1,176	2.231	0.347	0.498	0.047	0.060		-
35				12.75		1.590	3.036	0.468	0.678	0.063	0.081		1
40	2			16,616		2.066	3.966	0.607	0.885	0.081	0.106		
45						2.604	5.019	0.763	1.120	0.101	0.134		· · · ·
50			1823			3.203	6.196	0.938	1.383	0.124	0.166	0.033	0.037
60						4.589	8.922	1.340	1.991	0.176	0.239	0.047	0.053
70		-				6.221	12.144	1.814	2.711	0.238	0.325	0.063	0.073
80						8.102	15.862	2.359	3.540	0.308	0.425	0.081	0.094
90		-				10.229		2.976	4,481	0.387	0.538	0.102	0.115
100		-				12.604		3.663	5.532	0.476	0.664	0.124	0.14
125	1.4					19.624		5.694	8.644	0.736	1.037	0.192	0.229
150		<u>_</u>						8.169	12.447	1.053	1.493	0.273	0.330
175								11.089	16.941	1.426	2.032	0.369	0.449
200				- 14 H				14.454		1.855	2.654	0.480	0.586
250		2		- A - A						2.882	4.147	0.743	0.916
300	1.00	-								4.135	5.972	1.064	1.315
350				1.1						5.611	8.129	1.442	1.795
400						1.00		1.00		7.313	10.618	1.877	2.345
450				1.1			50.5			9.239	13.438	2.369	2.968
500				1.12						11.390	16.590	2,919	3.664
600										16.366		4.188	5.276
700		2										5.687	7.18
800		-										7.413	9.379
900				1.2			6 2 3	-		1.1	-	9.368	11.87
1000												11.552	14.65

**Figure 2.21** Pressure drop estimates for rigid and flexible transfer lines with liquid nitrogen. (Courtesy of PHPK Technologies, Inc.).

Since heat transfer and pressure drop follow Rayleigh's equivalence, a safe assumption is that the pressure drop caused by a component is about 1.24 times that of an equivalent length of pipe. Let us pick a pipe run of 500 ft of actual pipe with 24 components in it. The 24 components represent  $24 \times 1.24 = 30$  equivalent feet of pipe. The heat leak for this case is then

 $(530 \text{ ft of equivalent pipe}) \times [0.85 \text{Btu/hr ft}]) = 450.5 \text{ Btu total heat leak}$ 

The pressure drop for this case is

 $(530 \,\text{ft equivalent pipe}) \times (0.034 \,\text{psi/ft}) = 18 \,\text{psi}$ 

**Summary.** For this sample case, 500 ft of 2 in. I.D. pipe carrying liquid hydrogen with 24 fittings will have a heat leak of 450 Btu and a pressure drop of 18 psi, which is well within our stated parameters. Other cases are readily calculated in a similar manner.

## 6. COOLDOWN

The amount of liquid required for cooldown can be estimated rapidly by equating the sensible heat of a pipeline and its insulation to the heat of vaporization of the fluid. This, of course, does not consider heat leaking into the system, frictional losses, or changing temperature of the gas discharge from the system. Should any one of these items contribute a sizable heat load to the system, then the amount of liquid required for cooldown would obviously be low. In the final analysis, economics will normally be the most important factor in the selection of a piping system. Such economics will depend largely on the duration of the transfer and the time between transfers. These times must be evaluated rather closely if the economic evaluation is to be valid.

In Chapter 4, we will see that the heat capacity of all crystalline materials goes to zero as the absolute temperature goes to zero. Accordingly, the amount of cryogenic fluid needed for cooldown also goes to zero as the initial temperature of the solid goes to zero. In other words, prechilling a liquid hydrogen system with liquid nitrogen will save a lot of liquid hydrogen.

Figures 2.22–2.25 give cooldown values for nitrogen, oxygen, hydrogen, and helium. They are based on the heat capacity of aluminum (Al); stainless steel (SS), typically a 304 series; and copper. They all show that the amount of coolant per mass of metal decreases rapidly as the initial cooldown temperature decreases. For each metal, there is a pair of MAX and MIM curves. The MAX curve is the maximum amount of coolant required if only the heat of vaporization of the liquid is available to cool the metal. This is the worst case. The MIN curve is the minimum amount of coolant required if both the heat of vaporization of the respective liquid *and* all of the sensible heat capacity of the liquid turned gas are available to cool the metal. This is the best case and will occur only if all of the boil-off gas is somehow in perfect heat exchange with the metal being cooled, such that the boil-off gas vents at the same temperature as the warm metal. The vent gases must move slowly past the metal in order to achieve this "best case" cooling. In other words, all of the possible refrigeration is captured; none is wasted. Only by very careful and expensive design, such as in the cooling of some space satellites, is the minimum ever achieved.



**Figure 2.22** Cooldown to liquid nitrogen temperatures. Mass of liquid nitrogen required per mass of metal vs. starting temperature.



Figure 2.23 Cooldown to liquid oxygen temperatures. Mass of liquid oxygen required per mass of metal vs. starting temperature.

It is instructive to see just how much precooling a liquid hydrogen system with liquid nitrogen can help. Referring to Fig. 2.2 for hydrogen, we see that starting at 540°R ( $80^{\circ}$ F), it will take (MAX case) about 0.2 1b of liquid hydrogen to cool 1 lb of stainless steel to  $36^{\circ}$ R (20 K). Now suppose that the stainless steel system is precooled with liquid nitrogen to  $139^{\circ}$ R (77 K). The same MAX curve now predicts that only 0.01 1b of liquid hydrogen will be needed per pound of steel to cool it the rest of the way to  $36^{\circ}$ R (77 K). The liquid hydrogen use has been cut by a factor of 20. The price we pay (see Fig. 2.19) is that 0.4 1b of liquid nitrogen is used per pound of metal



**Figure 2.24** Cooldown to liquid hydrogen temperatures. Mass of liquid hydrogen required per mass of metal vs. starting temperature.



**Figure 2.25** Cooldown to liquid helium temperatures. Mass of liquid helium required per mass of metal vs. starting temperature.

for precooling from 540°R (300 K) to  $139^{\circ}$ R (77 K). Such a trade is very economical indeed.

# 7. SUMMARY

As one would expect, the basic principles of thermodynamics, heat transfer, and momentum transfer apply equally as well to cryogenic engineering as they do to all other fields of engineering. Appropriate use must be made of the sometimes unusual low-temperature properties of fluids and materials (see Chapter 3 and 4).

Simple engineering correlations, usually based on the behavior of a large number of near-room-temperature fluids, must be used with caution. Pressure drop correlations, for instance, are usually based on the flow of single-phase streams under steady-state conditions. Thus they may underestimate the pressure drop in cryogenic systems by 10-30% due to the high vaporization tendency of cryogenic fluids.

Finally, the usual modeling assumptions for normal engineering work may not apply. Cryogenic fluids are nearly always at their boiling point, are seldom adiabatic, and are often composed of two phases. Radiative heat transfer can seldom be neglected.

This is not to say that cryogenic systems cannot be rigorously modeled, for they can be, if one takes into account all of the peculiar properties of cryogenic materials and properties. Rather, correlations must be used with caution, and a return to basics is usually the safest approach.

# **3** Cryogenic Fluids

# 1. PVT BEHAVIOR OF A PURE SUBSTANCE

The relationship of specific or molar volume to temperature and pressure for a pure substance in an equilibrium state can be represented by a surface in three dimensions, as shown in Fig. 3.1. The shaded surfaces marked S, L, and G in Fig. 3.1 represent, respectively, the solid, liquid, and gas regions of the diagram. The unshaded surfaces are the regions of co-existence of two phases in equilibrium, and there are three such regions: solid–gas (S–G), solid–liquid (S–L), and liquid–gas (L–G).

Heavy lines separate the various regions and form boundaries of the surfaces representing the individual phases. Because of the difficulty of visualizing and drawing these surfaces, it is customary to depict the data on projections such as the PT and PV planes. Figure 3.2 is an example of a PT plane for water; other materials have similar diagrams.

The heavy line passing through points A and B marks the intersections of the two-phase regions and is the three-phase line, along which solid, liquid, and gas phases exist in three-phase equilibrium. According to the phase rule, such three-phase, single-component systems have zero degrees of freedom; they exist for a given pure substance at only one temperature and one pressure. For this reason, the projection of this line on the PT plane of Fig. 3.2 (shown to the left of the main diagram) is a point. This is known as a triple point.

The triple point is merely the point of intersection of the sublimation and vaporization curves. It must be understood that only on a P-T diagram is the triple point represented by a point. (On a P-V diagram it is a line.)

The phase rule also requires that systems made up of two phases in equilibrium have just one degree of freedom, and therefore the two-phase regions must project as lines on the PT plane, forming a P-T diagram of three lines—fusion (or melting), sublimation, and vaporization—which meet at the triple point.

The P-T diagram is divided into areas by three lines: the solid-vapor, solidliquid, and liquid-vapor lines. The *triple point* is a region in which liquid, solid, and vapor can exist in equilibrium simultaneously.

The P-T projection of Fig. 3.2 is shown to a larger scale in Fig. 3.3.

Upon projecting the surface on the *PT* plane, the whole solid-vapor region projects into the sublimation curve, the whole liquid-vapor region projects into the vaporization curve, the whole solid-liquid region projects into the fusion curve, and finally the "triple point line" projects into the triple point.