Chapter 1
Cryogenic Principles and Applications

Cryogenics is generally referred to as the science and technology of producing a low-temperature environment for applications. The word cryogenics has its origin in the Greek language where "kryos" means frost or cold and "gen" is a common root for the English verb to generate. Strictly speaking, cryogenics means to produce cold, yet the term has developed a more general connotation over years of usage by engineers and scientists. Today, the word cryogenics is associated with the production and study of low-temperature environments with a cryogenic engineer being a person who specializes in these areas. The expertise of a cryogenic engineer can vary considerably within this discipline. For example, he or she may be concerned mostly with heat transfer aspects of low-temperature fluids such as liquid hydrogen or helium or alternatively may be a specialist in methods of producing low temperatures such as various refrigeration technologies. Expertise in cryogenic engineering is in demand in a wide variety of technical fields including advanced energy production and storage technologies, transportation and space programs, and a wide variety of physics and engineering research efforts. As a result, the field is very interdisciplinary consisting of essentially all engineering fields focused on low temperature technology.

Over the years, the word cryogenics has developed several common usages. A cryogenic fluid is one that is used in the production of cold, while cryogenic machinery is the hardware used in achieving low-temperature environments. At first it would appear that all machinery and fluids used in cooling would be identified as cryogenic. However, it is generally accepted that the word cryogenics is reserved for those processes that take place below about 120 K. This distinction is somewhat arbitrarily established as it represents the point where permanent gases such as N_2, O_2, Ar and methane (CH_4) begin to liquefy. Sometimes cryogenics is used in reference to higher temperature processes such as cryo-preservation or cryo-surgery; however, these topics are outside the present discussion and therefore will not be considered as part of traditional cryogenics.

1.1 Temperature Scale

Assuming it is possible to refer to a range of temperature as being the cryogenic regime and that the range spans from absolute zero to about 120 K, one might ask the following question: "Why all the excitement over a range of temperature spanning only about a hundred kelvin?" The answer to this question lies in the thermodynamic description of the temperature scale.

One normally thinks of the process of producing low temperatures as reduction of entropy, where the entropy is a state function defined as,

$$s = \int_0^T \frac{dQ_R}{T} \tag{1.1}$$

with T being the absolute temperature and the entropy is taken to be identically zero at absolute zero. The third law of thermodynamics states that as absolute zero is approached, not only does the entropy of a system go to zero, but the entropy change associated with an adiabatic process must also go to zero. In other words, the lower the absolute temperature the more difficult it is to obtain a unit temperature decrease. Among other phenomena, this principle manifests itself in the thermodynamic efficiency of refrigerators decreasing with temperature.

It is therefore often more meaningful to identify temperature as having a logarithmic rather than linear scale. On a logarithmic temperature scale, the cryogenic range occupies a very large portion of achievable temperatures. Plotted in Fig. 1.1 is the temperature scale with the range of physical phenomena superimposed.

It should be immediately clear that cryogenic temperature range occupies nearly half of the achievable temperatures. From the physical point of view, this range is interesting for the large number of phenomena that occur within it. A few examples of these include: phase changes of many common elements, magnetic ordering, solid-state transformations, and the quantum effects including the onset of superconductivity and superfluidity.

A subfield of cryogenics is identified with the most permanent of all gases, helium. Although helium is a fairly rare element, there is probably more known about low temperature helium than any other fluid with the possible exception of water. Helium has a number of important applications in welding and lighter than air vehicles, but of greater interest to the present discussion is its use as a low temperature coolant. The refrigeration and liquefaction of helium are somewhat specialized fields because of the extremely low temperatures involved. However, the existence of low temperature helium enables a wide variety of technological applications. It is also a fluid with extremely interesting physical properties. These topics will be discussed in later sections.

The field of helium cryogenics spans a smaller range of temperature than classical cryogenics in part because the critical point of the most common isotope,
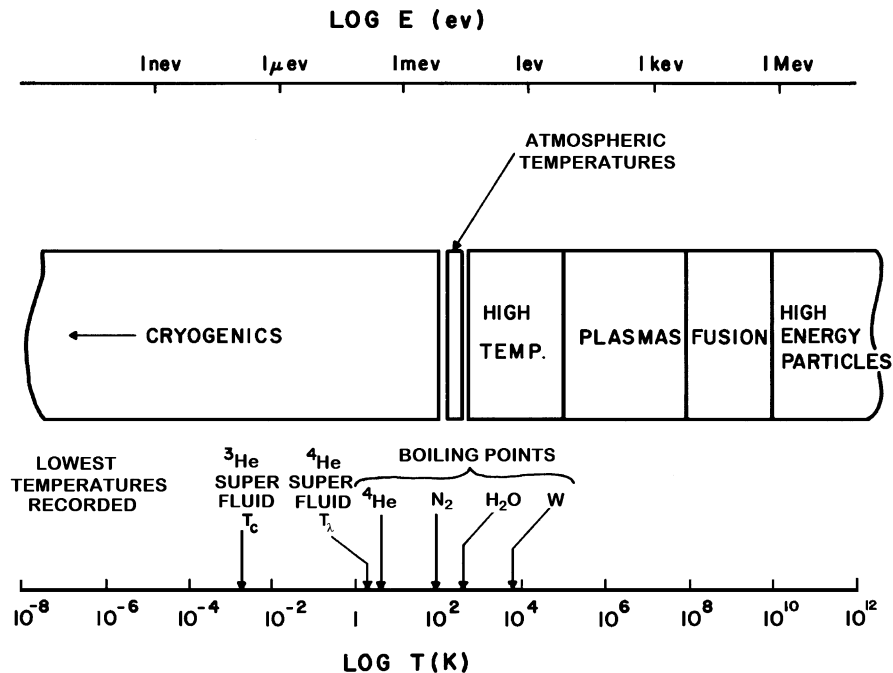
Fig. 1.1 Logarithmic temperature scale with superimposed physical phenomena. Note that $E = k_B T$ and 1 eV is equivalent to 11,609 K

^{4}He, is only 5.2 K. However, one of the more unique features of helium is that it does not solidify except under an external pressure exceeding 2.5 MPa (~25 atm) at low temperatures, thus allowing fluid properties to be studied to as low a temperatures as physically possible. At the present time the minimum achievable bulk temperature for liquid helium (in this case, the rare isotope ^{3}He) is below 100 μK. The technology of achieving these ultralow temperatures is special and relevant primarily to fundamental studies of condensed-matter and astrophysics. Since the emphasis of this book is on the technological applications of helium cryogenics, the phenomena associated with ultralow temperatures are not considered in much detail. Thus, helium cryogenics as described here emphasizes the range of temperature where the fluid has large scale potential applications as a coolant, 1 K ≲ T ≲ 10 K. In Chap. 9 we will consider helium cryogenics for temperatures below 1 K both in terms of the technology of achieving these temperatures as well as the physical phenomena that occur in this range. However, it is important to keep in mind that this regime is only accessible through the use of the rare isotope of helium (^{3}He).

1.2   Historical Background

Research and development into the field of cryogenics began more than 100 years ago. Perhaps the most significant discovery in that time frame was the realization that common fluids such as air and water have similar behavior when cooled to temperatures near their respective critical points. In the early 1860s, substantial theoretical and experimental evidence was put forth identifying the concepts of phase separation and critical phenomena [1]. These ideas, which are mostly taken for granted today, form essential background to the understanding and application of the liquefaction and refrigeration processes.

To summarize phase separation and critical phenomena, reference is made to a useful general figure (Fig. 1.2) showing the states of matter when temperature T is plotted versus entropy S. Here the critical temperature T_c is the maximum of the two-phase coexistence region, which for obvious reasons is often refer to as "the dome".

As a rule of thumb, the normal boiling point T_{nbp} of a liquid is about $T_c/2$, although there is considerable deviation from this rule particularly for cryogenic fluids like helium where $T_{nbp}/T_c \approx 0.8$.

Three major scientific developments in the late nineteenth century provided the essential framework for the successful liquefaction of helium and thus the beginning of helium cryogenics. The first of these occurred during the study of low temperature O_2 in 1877 by two separate investigators in Europe, Cailletet in France and Pictet in Switzerland. Each of these workers demonstrated the concepts of liquid–vapor coexistence in permanent gases near their normal boiling point. Furthermore, Pictet's method used the cascade principle to produce liquid O_2,
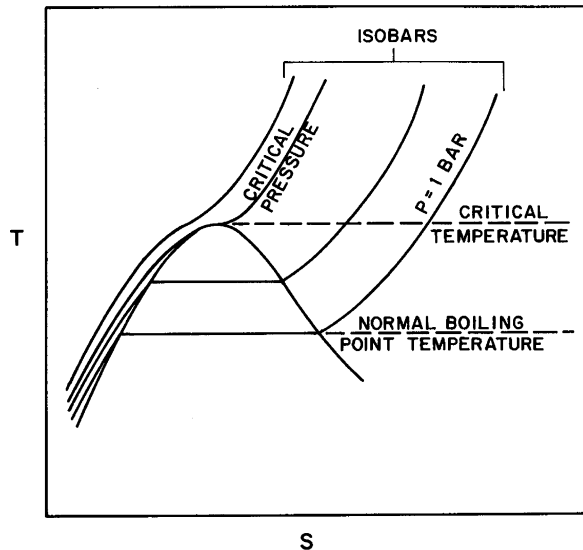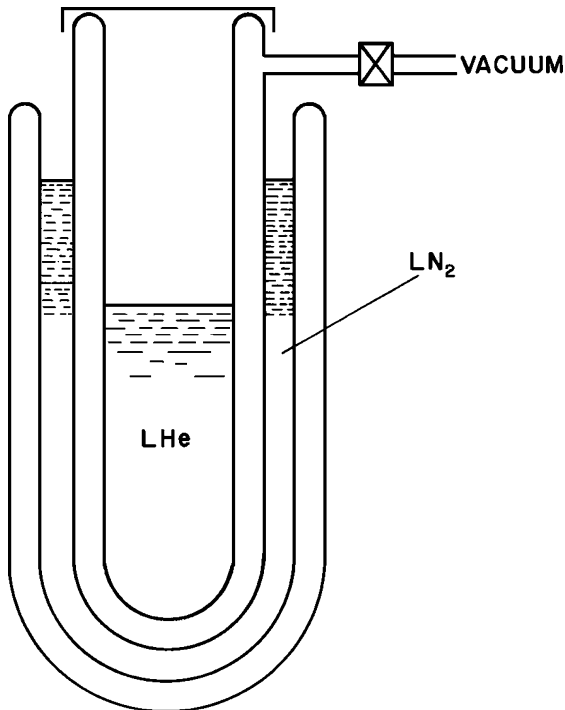

Fig. 1.2 Typical temperature-entropy diagram for a pure substance

Fig. 1.3 Schematic of an early dewar vessel for containing liquid helium. The outer liquid nitrogen dewar provides a thermal radiation intercept

where gases are successively cooled to lower temperature by exchanging heat with a higher normal boiling point liquid. This method is later used in the first successful liquefaction of helium by H. K. Onnes.

The second major development occurred in 1892 when Sir James Dewar of the Royal Institution in London introduced the vacuum insulated flask as a storage container for liquid cryogens. His concept, which consisted of a glass double-walled vacuum vessel with inner walls silvered to reduce thermal radiation heat transfer, finally allowed collection of a significant quantity of liquid cryogen. A drawing of a simple "dewar" vessel that could be used for liquid helium is shown in Fig. 1.3. In this case, liquid nitrogen shielding is provided to reduce further the thermal radiation heat leak.

The dewar is essential for the storage of liquid helium because of the fluid's extremely small latent heat. Modern liquid helium dewars are significantly more sophisticated than that shown in Fig. 1.3, but they still use vacuum and highly reflective surfaces to achieve efficient thermal insulating systems.

Sir James Dewar made the final development that led the way to the liquefaction of helium when he demonstrated the use of a Joule-Thomson valve to produce liquefaction of hydrogen, the last of the permanent gases with boiling points above that of helium. It is particularly significant that Dewar employed a Joule-Thomson valve, which produces essentially an isenthalpic expansion, because this method also can be used in the production of liquid helium. With liquid hydrogen available

(with a normal boiling point $T_{nbp} = 20.4$ K), it became possible to consider liquefying helium by a combination of the cascade principle and Joule-Thomson expansion. The chief remaining difficulty was that helium gas was a rare commodity around 1900.

It took another 10 years for helium to be successfully liquefied. At the time, two laboratories were vying to be the first to accomplish the task: Sir James Dewar's lab in London and H. Kamerlingh Onnes lab at the University of Leiden. For a variety of technical reasons, the Onnes group came out on top in the competition successfully achieving liquefaction of helium in 1908. At that time their total helium inventory in their lab was only 360 STP gaseous liters (equivalent to about 0.5 liquid liter), and yet as a result of this early success the Leiden rapidly became the world-wide center of liquid helium research. Among the achievements attributed to Onnes' group are included the discovery of superconductivity in many of the elements.

For the next 30 years, production of liquid helium and its associated research and applications were limited primarily to a few specialized laboratories. Researchers actively investigated the properties of materials as well as those of liquid helium down to temperatures below 1 K. Included among their discoveries are: super-fluidity in ^{4}He, identification of numerous superconducting materials, and the use of magnetic cooling to achieve temperatures below 1 K. At the same time, researchers envisioned large-scale applications of helium cryogenics but lacked the motivation and resources to develop these technologies.

In the 1940s commercial development of hydrogen and helium liquefaction equipment began, owing to a large extent to the efforts of Prof. Samuel Collins of MIT and the Arthur D. Little Company. For the first time, laboratories could purchase helium liquefaction plants and liquid helium become available on the open market. Liquid helium research became more widely practiced. This point in time marked the beginning of large-scale cryogenic engineering, which required individuals skilled at design and handling of cryogenic equipment. At first, military and space applications led the field. Later major thrusts in applications of super-conductivity began to dominate low temperature applications. As a result of this growth, helium cryogenic engineering has developed into a substantial discipline.

Since the development of commercial helium refrigerators, major progress has been made on the two fronts of research and development. In basic research, the ready access to large quantities of liquid helium has freed the researchers to push toward lower temperatures. Milestones in this progress must include: the development of ^{3}He-^{4}He dilution refrigeration technology permitting continuous cooling in the millikelvin temperature range; the approach to submillikelvin temperatures using techniques such as Pomaranchuk cooling and nuclear demagnetization; and the discovery of superfluidity in ^{3}He at about 2 mK.

Commercial development has also progressed substantially since the 1940s. Larger and larger liquefiers and refrigerators are being produced. Huge helium liquefaction plants with capacities in the 1,000s of liters/hour operate in various parts of the world separating helium from its primary source in natural gas wells. Supplying liquid helium for superconductivity applications has similarly increased

in scale and sophistication. Installations like the Large Hadron Collider particle physics experiment at CERN in Geneva, Switzerland now have fully automated refrigeration plants in the multi-kW range supplying liquid as well as cold gas helium to a variety of thermal loads within the accelerator facility. In addition to these larger-sized refrigerators, there has also been broad and extensive development of small stand-alone refrigerators, or cryocoolers, with cooling capacities in the 1–100 W range for cooling a wide variety of low-power applications including superconductors and infrared detectors.

Overall, helium cryogenics has now evolved into a well-established discipline providing the environment for a wide range of technologies. What is in store in the future? Trends include development of a wider range of standard products both from the very small refrigerators to the largest ones. New demands are being placed on the systems being produced: higher thermodynamic efficiency, greater reliability, and cleaner operation, and lower cost. Considerable research is aiding this progress and new technologies such as applications of high temperature superconductors are putting special demands on helium cryogenic systems. There continues to be unique and challenging applications that require low temperatures and cryogenic facilities. Thus, there is a steady demand for engineers and scientists with cryogenic engineering skills.

1.3   Applications for Cryogenics

As motivation to the discussion of the properties and production of low-temperature fluids, it is useful to identify the major applications for cryogenics technology today. Some of these are commercial enterprises, while others are still primarily in the stages of research and development. It is possible to separate these applications into at least six major categories:

1. Storage and transport of gases
2. Separation of gases
3. Biological and medical applications
4. Altering material properties by reduced temperature
5. Electronics
6. Superconductivity

Large-quantity storage and transport of gases are best achieved with the help of cryogenics. It is much more efficient from the standpoint of total weight, to transport cryogenic fluids in the liquid state rather than as a pressurized gas. Furthermore, the gases evolved from a storage dewar can maintain a lower impurity content than is common in high-pressure gas storage. There are a number of examples where cryogenic storage and transport are widely practiced. At relatively high temperatures, liquid natural gas (LNG) is transported on a large scale in tanker ships containing over 100,000 m^3 of liquid. Liquid oxygen is stored in large quantities for applications in steel production as well as to provide high-purity

gaseous oxygen supplies for hospitals. Another major application for cryogenic storage and transport is in liquid fuel rockets where LO_2 and LH_2 are common propellants. Even helium is often transported in the liquid state. This is not only because many users do not possess the necessary liquefaction equipment but also to save weight for transportation.

The separation of gas mixtures such as air or natural gas is a commercial enterprise in which cryogenics plays a major role. By using the physical properties of adsorption, that is, the tendency for gases to condense on cold surfaces, it is possible to separate gas mixtures by differences in their adsorption rates. This procedure is used commonly in extracting O_2 and N_2 from air, for purification of LNG or separation of rare gases such as Ne or He. Related to gas separation is the technology of cryopumping, where the physical process of adsorption provides a mechanism for clean, oil free, high-speed pumping systems. For this process to be effective, the pumping surfaces must be well below the critical temperature of the gas to be pumped.

Biological and medical uses for cryogenics are extensive. In these applications the goal is to store, modify, or destroy a biological structure by reducing its temperature. Storage of cellular structures in liquid nitrogen is a common practice, the largest of these being the storage of blood plasma. Other examples of this technology include storing cattle semen for artificial insemination and the preservation of food. Apart from cellular storage, medicine is making increasing use of cryogenics. In a procedure known as cryosurgery, selected areas of tissue are frozen and removed with less difficulty or trauma to the patient than by conventional surgical methods. Such techniques are commonly experienced by almost anyone who has visited a dermatologist.

The basic properties of materials change as the temperature is reduced and these effects are used in several engineering applications of cryogenics. A good application for material property variation is in the recycling industry. Cryogenic recycling uses low temperatures to separate materials. The approach takes advantage of differential thermal contraction and the increased brittle nature of materials at low temperatures. There are numerous examples of composite materials that can be recycled by this method. Thermal contraction can also be used in the construction of mechanical structures. The assembly of a close tolerance connection can be facilitated if one of the components is first cooled in a cryogenic fluid to make it slightly smaller. In these applications there is little need to reduce the temperature below the normal boiling point of liquid nitrogen because very little thermal contraction occurs below this temperature.

Besides mechanical properties, low temperatures also are used to change electrical properties of materials. One of the major applications of this process is in the cooling of detectors and other electronic sensors. The low temperature reduces the thermal noise and provides an isothermal environment for the sensor. Examples of devices that use low temperatures include infrared detectors for everything from night vision equipment to large-scale astrophysical science experiments.

The technology of superconductivity warrants special attention as an application that depends on cryogenics. The largest-scale application of superconductivity is in

magnet technology. At present, superconducting magnets are an integral part of high-energy physics accelerators, magnetic fusion confinement systems, energy storage, magnetic levitation, whole-body magnetic resonance imaging (MRI) scanners as well as specialized research magnets. Additionally, RF particle accelerators us superconducting Nb cavities that must be cooled to low temperature (T ~ 2 K) to achieve the required performance. Most of these systems operate at low temperature (T < 10 K) and thus require fairly complex helium refrigeration systems.

The discovery and development of high temperature superconductors has significantly impacted the development of cryogenic systems. Large-scale HTS superconducting applications such as are proposed for the power industry are now contemplated to operate at significantly higher temperatures, T > 30 K. Small-scale applications of HTS are also being developed many of which only require a few watts of cooling. These applications have had a major impact on the development of small-scale, intermediate temperature refrigeration systems. The development of cryocoolers for such applications has been an active thrust area of the field in recent years.

1.4   Thermodynamic Laws

Thermodynamic principles and concepts are of fundamental importance to the field of cryogenics. Thermodynamics forms the basis for calculations of the properties of cryogenic fluids as well as the performance of refrigeration and liquefaction systems.

There are three basic laws of thermodynamics that apply to all systems and are of particular interest to the discussion here. Although it is assumed that the reader is familiar with these laws through a previous course in thermodynamics, for completeness and commonality of notation a review of the subject is presented here. For further details, the reader should consult one of many thermodynamics text books.

1.4.1   First and Second Laws of Thermodynamics

The first law of thermodynamics involves conservation of energy in a closed system. Consider two thermodynamic states characterized by their internal energy, E_i and E_f. If we connect these two states by an adiabatic path, that is a process taking the system from one thermodynamic state to another without the production or absorption of heat, the work W needed is exactly equal to the change in the internal energy. This statement can be considered a definition of work; that is, work done on an adiabatic system is equal to the increase in the potential energy.

Fig. 1.4 Adiabatic paths
between two thermodynamic
states
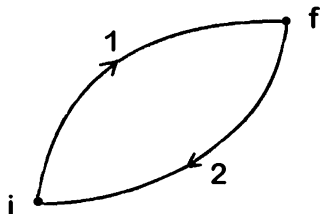
On the other hand, if the process is not adiabatic, an amount of heat Q is
produced during the process and conservation of energy demands that the amount
of extra heat be included in the total amount of work done. This statement leads to
the mathematical formulation of the first law of thermodynamics which is written,

$$Q = E_f - E_i + W \tag{1.2}$$

It is important to keep in mind that the internal energy is a state function and its
change only depends on the initial and final points of a path in thermodynamic
space. This is to be compared to the heat and work functions which are path
dependent.

Now consider a cyclic process where a system in question is taken from the
initial state through the final state and back to the initial state by some other path.
This process, shown schematically in Fig. 1.4, may be a heat engine or a cycle used
to refrigerate a cryogenic fluid. The principal distinction between an engine and a
refrigerator is with the sign of the work process. Since the cycle closes on itself, the
change in internal energy (ΔE) around the cycle is zero and the first law (1.2)
demands that the difference between the heat and work for the two paths must be
equal in magnitude but opposite in sign. For the entire cycle, the sum of the heat and
work must be identically zero. However, the amount of work that must be done to
accomplish the cycle is proportional to the enclosed area in Fig. 1.4. The larger the
area, the more work that is done per cycle and in turn the larger amount of heat that
must be generated.

Before discussing the other thermodynamic laws, it is useful to go into a little
more detail about the work as part of a thermodynamic process. To make the first
law into a more useful form for application, the initial and final states can be
brought arbitrarily close together resulting in the differential form of the first law,

$$dQ = dE + dW \tag{1.3}$$

For a thermodynamic process, the differential work term dW in (1.3) can take on
several forms, dependent on what type of system is of interest. Of particular interest
to cryogenics are:

Liquid–gas system:

$$dW = p \, dV \tag{1.4a}$$
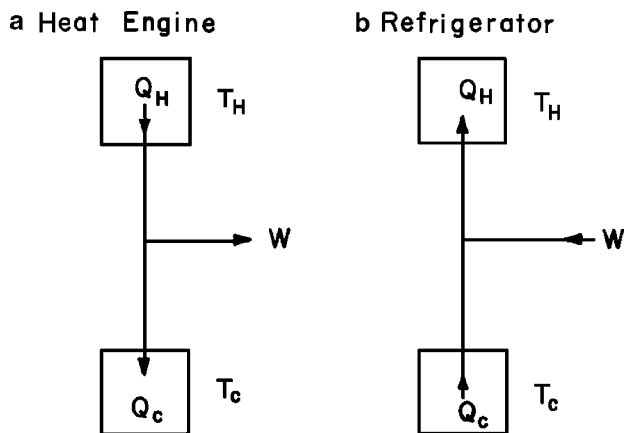
a Heat Engine   b Refrigerator

Fig. 1.5 Schematics of a heat engine and a refrigerator

Magnetic system:

$$dW = -\mu_o \, \mathbf{H} \bullet d\mathbf{M} \qquad (1.4b)$$

Electric system:

$$dW = -\mathbf{E} \bullet d\mathbf{P} \qquad (1.4c)$$

The *pdV* work term is the most common since most refrigerators use gas cycles. However, magnetic refrigerators have special applications, which will be discussed in later sections. Note that the latter two differentials are vector quantities dependent on the direction of the applied fields, while the *pdV* product is directionally independent. Fortunately, it is a rare occurrence for more than one type of work to be important in a particular system or process. The differential form of the first law is preferred in process calculations as the process variables usually change continuously within the cycle.

Moving on, the second law of thermodynamics is concerned with the conversion of heat into work and the efficiency with which this can take place. The second law works in concert with the first law to describe correctly the behavior of an ideal thermodynamic process. The second law is often defined in terms of heat engines and their performance of work [1]:

> It is impossible to construct an engine that does work while exchanging heat with only one reservoir.

Thus, according to the second law, any engine that performs work must have at least two reservoirs. By analogy, a refrigerator, which is simply an heat engine running in reverse, also requires two reservoirs; the low temperature one from which heat is absorbed and the high temperature one into which heat is rejected. Schematic configurations of a heat engine and a refrigerator are shown in Fig. 1.5.

The attached subscripts refer to the hot (H) and cold (C) reservoirs. Note that the engine supplies work while the refrigerator requires work to complete the process.

The combined first and second law therefore require an engine or refrigerator to operate between two reservoirs at different temperatures. For an engine, the thermodynamic efficiency η for such a process is given in terms of the work output W divided by the heat input, Q_H.

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} \tag{1.5}$$

Note that we have used the first law for the thermodynamic cycle to replace W with $Q_H - Q_C$, which explicitly shows why η must always be less than unity. It is apparent that an efficiency of unity can never be achieved because the second law requires two reservoirs and Q_C is always finite.

For a refrigerator, the important quantity to optimize is the coefficient of performance (COP), which is defined as the ratio of the heat extracted from the low temperature reservoir to the work done on the system,

$$COP = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C} \tag{1.6}$$

Thus the COP is just the inverse of the efficiency. For the case of an engine, the work done is given by the area enclosed by the cycle and the heat is expelled at T_C. On the other hand, for a refrigerator, the heat is expelled at T_H and the cycle uses the work to extract heat at T_C.

The entropy S is a state function that is commonly used in cryogenic systems because it better defines the process variable that one is trying to minimize. For example, the most efficient process available for refrigeration is isentropic, $\Delta S = 0$ and this is only achievable if the processes are fully reversible. On the other hand, if the process is done irreversibly (such as Joule-Thomson isenthalpic expansion) or with exchange of heat, then $\Delta S > 0$ and there is entropy generated. The Clausius theorem, which is part of the second law, refers to the entropy associated with a closed cycle. If such a cycle follows reversible paths, the Clausius theorem states that the entropy change through the cycle is identically zero.

Like all thermodynamic variables, entropy also has a definition based on statistical mechanics. The statistical definition of entropy is associated with order in the system. The greater the order the lower the entropy. Thus, a condensed liquid is in a lower entropy state than its coexisting vapor. Normally, the solid state of a substance is in a lower entropy state than the liquid state because the crystal periodicity implies a more ordered system. In a magnetic system, if the spins are all aligned with the applied magnetic field they are more ordered and in a lower entropy state than if they are randomly oriented. This would suggest that if absolute zero were attainable, the system would be completely ordered, i.e. all the spins would be aligned and the solid would be perfectly periodic. Helium is an exception to this general rule, as will be discussed later, because of its quantum nature the lowest entropy state of helium is liquid.

Fig. 1.6 Carnot cycle
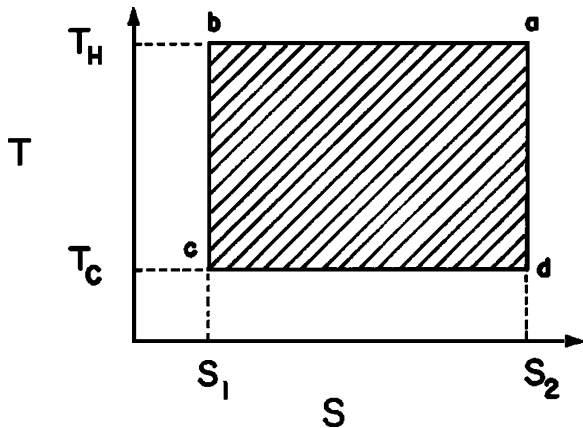
In statistical mechanics, the definition of entropy evolves from introduction of a thermodynamic probability function Ω, which is a measure of the occupation of the states in the thermodynamic system. Entropy is given mathematically by a function of this probability,

$$S = k_B \ln \Omega \qquad (1.7)$$

where k_B, is the Boltzmann constant equal to 1.38×10^{-23} J/K molecule. Incidentally, other state functions of the system are also defined in terms of Ω. The statistical definition of entropy leads to a natural physical understanding of absolute zero temperature. At absolute zero, the system is in a ground state with the probability of that state being occupied at unity. Consequently, the probability function is equal to unity ($\Omega = 1$) and by the definition in (1.7) $S_0 \equiv 0$.

A useful application of the entropy concept is obtained by considering a Carnot refrigerator. The Carnot cycle is shown schematically by the four-step process in Fig. 1.6. The first step in the cycle takes the thermodynamic system isothermally (at constant temperature) from (a) to (b), decreasing the entropy from S_2 to S_1. This process could be for example the isothermal compression of a gas at high tempera- ture. The second step is an isentropic process (constant entropy) that reduces the temperature of the system from T_H to T_C, taking it from (b) to (c). The third step then heat exchanges with the low-temperature reservoir, a process (c) to (d) that takes place isothermally. Finally, the cycle is completed by an isentropic return to the original point (a). Since the Carnot cycle is reversible the work done is equal to the area enclosed by the cycle. The amount of heat absorbed from the low-temperature reservoir is $Q_C = T_C \Delta S$ and the heat ejected in the hot reservoir is $Q_H = T_H \Delta S$. Therefore, for a Carnot cycle the ratio of Q_C to Q_H is simply the ratio of absolute temperatures,

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H} \qquad (1.8)$$

From (1.6), it is easy to show that the *COP* of a Carnot refrigerator is,

$$COP = \frac{T_C}{T_H - T_C} \tag{1.9}$$

The ideal Carnot refrigerator is used as a comparative standard for practical refrigeration systems. Any real refrigeration system operates at a fraction of Carnot performance due to the non-ideal nature of the processes involved in the cycle.

1.4.2   Third Law of Thermodynamics

The unattainability of absolute zero, the third law of thermodynamics, has fundamental significance in numerous aspects of cryogenics. Since the difficulty in achieving low temperatures increases as the temperature is decreased, cryogenics, by definition, is an attempt to fight this thermodynamic law. Additionally, the third law helps us understand the behavior of thermodynamic variables as absolute zero is approached. For example, considering an isothermal change in pressure in a liquid–gas system, we can express the entropy change as

$$S(T,p) - S(T,0) = -\int_0^p \left(\frac{\partial V}{\partial T}\right)_p dp \tag{1.10}$$

an expression obtained by integrating one of Maxwell's relations [1]. Similarly, for a magnetic system, an isothermal change in magnetic field leads to the following expression:

$$S(T,H) - S(T,0) = \mu_0 \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \tag{1.11}$$

where M is the magnetization of the material. By combining (1.10) and (1.11) with the third law of thermodynamics a statement can be made about the behavior of V and M as absolute zero is approached. Specifically, since ΔS approaches zero as $T \to 0$, both the volume and magnetization must approach constant values.

In addition to the above conventional statement of the third law and unattainability of absolute zero, the Nernst-Simon statement concerns itself specifically with entropy change [1]:

> Entropy change associated with an isothermal reversible process in a condensed system approaches zero as $T \to 0$.

Since the Nernst-Simon statement deals only with the entropy change, the absolute entropy of a system at $T = 0$ must be a universal constant. It can be shown further that this constant can arbitrarily be set identical to zero.
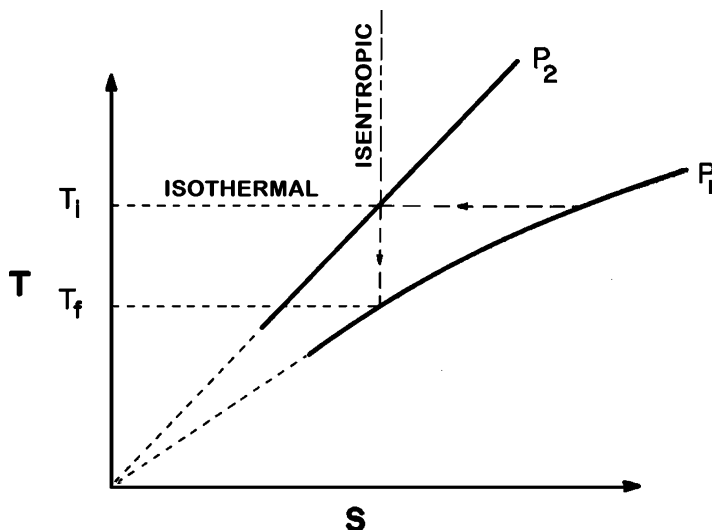
Fig. 1.7 Schematic T-S diagram showing isothermal and isentropic properties

The unattainability of absolute zero can be demonstrated by a number of examples. One useful example is based on the Nernst-Simon statement of the third law $(\Delta S \to 0)$. Consider the schematic T-S diagram in Fig. 1.7 showing two isobars (constant pressure curves). For this type of system, it is fairly straightforward to achieve cooling and reduce the temperature by performing a constant entropy (isentropic) expansion from T_i to T_f. It would appear possible to extend this procedure toward absolute zero by a repeated application of isothermal compression from p_1 to p_2 and subsequently isentropic expansion from p_2 to p_1. However, the third law states that $\Delta S_0 = 0$ so the two isobars must approach the same value of the entropy at $T \to 0$. Thus, it should take an infinite number of steps to reach absolute zero by this process.

These concepts are integral to the processes and properties that make up cryogenic systems. In engineering systems operating near room temperature, it is common to treat many of the process variables as constants or at least as simple functions of temperature. These kinds of simplifications are generally not suitable for cryogenic system analysis as will become clear in subsequent sections of this book.

Questions

1. Why is it more efficient to store and transport industrial gasses as cryogenic liquids?
2. What are the principal differences between a heat engine and a refrigerator?
3. What does the third law of thermodynamics tell us about the heat capacity of a solid as T approaches 0 K?

4. Show that the thermodynamic definition of entropy leads to a logarithmic temperature scale.
5. Compare T_b/T_c for some common cryogenic fluids. Comment on the relative values.

Further Readings

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