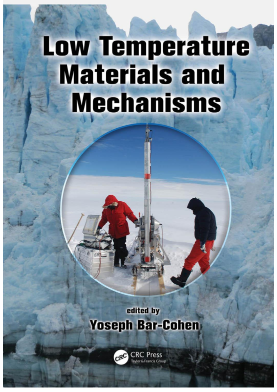

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1

Introduction to Low Temperature Materials and Mechanisms

Yoseph Bar-Cohen and Ray Radebaugh

CONTENTS

1.1 Introduction

Operating at low temperatures is essential to many processes in numerous fields of science and engineering including refrigeration, space exploration, electronics, physics, chemistry, thermodynamics, and medicine [Barron, 1985; Gutierrez et al., 2000; Halperin, 1995; Kent, 1993; Pobell, 2007; Weisend, 1998]. There is a growing interest in technologies that are applicable at low temperatures for planetary exploration of bodies in the solar system that are extremely cold. These include potential NASA *in situ* exploration missions to Europa and Titan where ambient temperatures are around –200°C. Elsewhere, as a method of slowing or halting chemical and biological processes, cooling is widely used to preserve food and chemicals, as well as biological tissues and organs. Furthermore, cooling is used to increase electrical conductivity leading to superconductors that enable such applications as levitation, highly efficient electromagnets, and so on. The subject of low temperature materials and mechanisms is multidisciplinary including chemistry, materials science, electrical engineering, mechanical engineering, metallurgy, and physics. This book covers some of the key aspects of the field including the chemistry and thermodynamics (Chapter 2), materials science (Chapter 3), the methods of characterizations (Chapter 4) as well as nondestructive testing and health monitoring (Chapter 5), the methods of cooling to cryogenic temperatures (Chapter 6), actuation materials and mechanisms (Chapters 7 and 8), instruments for planetary exploration (Chapter 9), methods of drilling in ice (Chapter 10), applications to medicine and biology (Chapter 11), low temperature electronics (Chapter 12), applications to fields of physics (Chapter 13), as well as other applications and challenges to the field (Chapter 14). Given the health hazards that are associated with working at cryogenic temperatures, a chapter has been dedicated to this topic as well (Chapter 15).

1.2 Cryogenic Temperatures

Cryogenics is the science and engineering of creating and investigating low temperature conditions [Scurlock, 1993; Kittel, 1996; Flynn, 1997; Radebaugh, 2002; Callister and Rethwish, 2012]. The word cryogenics is derived from the Greek words *kryos*, meaning “frost” or “cold,” and *–genic,* meaning “to produce.” Until around the mid-eighteenth century, it was believed that some gases could not be liquefied—these were named permanent gases. These gases were carbon monoxide, hydrogen, methane, nitric oxide, nitrogen, and oxygen, with the maximum attention given to the primary constituents of air—oxygen and nitrogen.

The temperature scale that is based on absolute zero with units in the same size as the Celsius degree is known as units Kelvin and is abbreviated as K. This symbol of the Kelvin unit was adopted in 1968. In the absolute, or Kelvin, scale, the lowest temperature is written as 0 K (without a degree sign). The Rankine scale with the symbol R represents the English absolute scale and has the same unit increments as the Fahrenheit scale.

Although cold temperatures can include temperatures at the level of water freezing (0°C), the term “cryogenic environment” refers to the temperature range below the point at which the permanent gases begin to liquefy. The term was applied initially to temperatures from approximately –100°C (–148°F) down to absolute zero Kelvin [Shachtman, 1999], and today the definition is related to temperatures below approximately –150°C (–238°F). In 1894, Onnes, of the University of Leiden, the Netherlands, was the first to coin the term “cryogenics” as the science of producing very low temperatures to liquefy the gases that were considered permanent [Onnes, 1894]. The English physicist Michael Faraday was one of the most successful in liquefying permanent gases; by 1845, he had managed to liquefy most of the permanent gases known at that time [Ventura and Risegari, 2007]. He liquefied the gases by cooling them via immersion in a bath of ether and dry ice and then pressurizing until they reached the liquid state. The liquefaction of air was accomplished in 1877 by Louis Cailletet in France and by Raoul Pictet in Switzerland [Timmerhaus and Reed, 2007]. In 1898, the liquefaction of hydrogen was successfully accomplished by the Scottish chemist James Dewar. In 1908, successful attempts on the last remaining gas element to be liquefied, helium, were carried out by Onnes at 4.2 K [Soulen, 1996].

The measurement of cryogenic temperatures requires methods that are not commonly used in daily life. The commonly used methods are mostly based on the use of mercury or alcohol thermometers, and these two fluids freeze and become useless at such low temperatures. Platinum resistance thermometers are based on the relation between electrical resistance and temperature and these provide relatively accurate measurements down to about 20 K. For temperatures down to 1 K and below, measuring the electrical resistance of certain semiconducting materials, such as doped germanium, also provides temperature gauging, but these thermometers require calibration over the range of temperatures at which the measurements are needed. The calibration of such secondary thermometers is done against the primary ones and they are based on measuring physical variable changes for which the response is determined theoretically.

The temperature of a material is a measure of the energy that it contains, which occurs in various forms of motion among the atoms or molecules that make up the material [Enss and Hunklinger, 2005]. A gas at a lower temperature has slower-moving atoms and molecules than gases at higher temperatures do. The possibility that a material can have a state at which all forms of motion are halted was predicted in 1848 by the English physicist William Thomson, later known as Lord Kelvin. The absence of all forms of motion would result in a complete absence of heat and temperature; this condition was defined by Thomson as absolute zero, which is equal to –273.15°C (–459.67°F). With the advent of quantum mechanics in the early twentieth century, we now know that at absolute zero some atomic motion still exists in materials, but it is in the lowest possible energy state, known as the ground state. Much of low temperature physics involves the study of materials close to the ground state where unusual behavior can occur.

1.3 Materials at Low Temperatures

The mechanical and electrical properties of many materials significantly change at temperatures that are in the range below 100 K; for example, most plastics, rubber, and some metals become brittle [Russell, 1931; Teed, 1952; Chapters 2 and 3]. Moreover, many metals and ceramics exhibit the phenomenon of superconductivity, which is the loss of all resistance to the flow of electricity [Seeber, 1998; Tsuneto and Nakahara, 2005]. Another phenomenon that takes place at temperatures very close to absolute zero is the state of superfluidity. Specifically, at 2.17 K helium becomes superfluidic, allowing it to flow through significantly narrower passages without exhibiting friction than associated with being in this quantum mechanical ground state [Tsuneto and Nakahara, 2005]. At temperatures below 2.17 K, helium has zero viscosity and produces a film that can creep upward over the walls of an open container. Superfluid helium also has an extremely high thermal conductivity, which makes it useful in cooling superconducting magnets. Another material property of great interest is the boiling point of various gases (see Table 1.1). In Chapter 3, the subject of materials and their properties at low temperatures is covered in greater detail.

1.4 Cooling to Cryogenic Temperatures

The tools that allow materials to reach cryogenic temperatures are called cryocoolers. Generally, there are four basic methods of reaching cryogenic temperatures [de Waele, 2011; Kittel, 1996; Barron, 1999; Kakaç et al., 2003; Chapter 6]:

a. Heat conduction—When two bodies are in contact, heat flows from the body at a higher temperature to the one at a lower temperature. Generally, conduction

TABLE 1.1

The Boiling Point of Various Gases

Gas Element	K	°C	°F
Argon	87	–186	–302
Helium	4.2	–269	–452
Hydrogen	20	–253	–423
Krypton	120	–153	–242
Neon	27	–246	–411
Nitrogen	77	–196	–320
Oxygen	90	–183	–297
Xenon	166	–107	–161

takes place among all forms of matter, that is, gas, liquid, or solid. Materials can be cooled to cryogenic temperatures by immersing them directly in a cryogenic liquid or by placing them in an atmosphere that is cooled by cryogenic refrigeration. In each of these techniques, the material is cooled by transferring heat (via conduction) to the colder material or the surrounding environment.

b. Evaporative cooling—This is also a commonly used method of cooling. Atoms and molecules move faster in the gas state than in the liquid state. When thermal energy is added to the particles in a liquid so they become gas, the remaining liquid is cooled. The gas is then pumped away and, as more heat is added, more liquid particles are converted into gas. The longer this process continues, the more heat is removed from the liquid, and the lower the temperature that is reached, as long as the pressure above the liquid is continually reduced. When the desired temperature is reached, the pumping is continued at a slower rate to allow maintenance at the specific low temperature. This method can be used to reduce the temperature of liquid nitrogen to its freezing point as well as to lower the temperature of liquid helium down to approximately 1 K.

c. Cooling by rapid expansion—This method uses the Joule–Thomson, or throttling, process and is the method of cooling that is most widely applied in household refrigerators and air conditioners, although it is also used in heat pumps and liquefiers. Cooling is achieved by expanding a gas or liquid through a valve or porous plug that is insulated from exchanging heat with the environment. In this process, the gas is first pumped into a container under high pressure. When a valve is opened, the gas escapes and expands quickly, and the temperature of the gas drops. The cyclic process involves continuous evaporation and condensation of a fixed amount of refrigerant in a closed system (see Figures 1.1 and 1.2). The evaporation takes place at a low temperature and low pressure, while the condensation takes place at a high temperature and high pressure. Thus, heat is transferred from an area of low temperature to an area of high temperature. This thermodynamic cycle involves compression of the vaporized refrigerant at constant entropy, which exits the compressor superheated. The superheated vapor travels through the condenser that cools it and removes vapor superheat, and then the vapor is condensed to a liquid by removing additional heat at constant pressure and temperature. The liquid refrigerant travels through the expansion valve, which rapidly reduces its pressure and causes evaporation of refrigerant to a mixture of liquid and vapor that travels though the evaporator coil until it is completely vaporized and cools the warm space by using a fan across the evaporator. The resulting refrigerant vapor returns to the compressor inlet, thus completing the thermodynamic cycle. In Figure 1.1, the aforementioned steps are taking place as follows: 1 to 2—the vapor is compressed; 2 to 3—superheat is removed from the vapor in the condenser; 3 to 4—the vapor is converted to liquid in the condenser; 4 to 5—the liquid is flashed into liquid and vapor across the expansion valve; and 5 to 1—the liquid and vapor are converted to a fully vapor state in the evaporator. Using this process with many stages, Onnes, in 1908, was able to liquefy gases such as helium down to 4.2 K.

d. Adiabatic demagnetization—This method provides a means for reaching temperatures much less than 1 K. The adiabatic demagnetization phenomenon uses paramagnetic salts that consist of a very large collection of magnetic particles with random polarity. The salt is placed in the magnetic field and it causes alignment of its magnetic particles. If the external magnet is removed and the paramagnetic

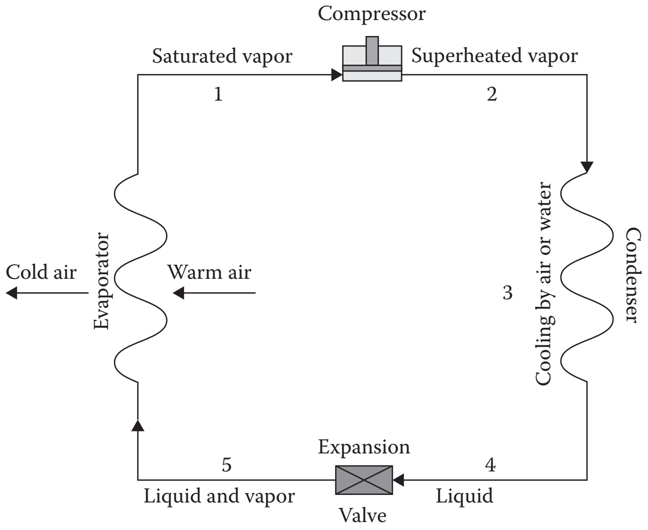

FIGURE 1.1
Typical vapor-compression refrigeration.

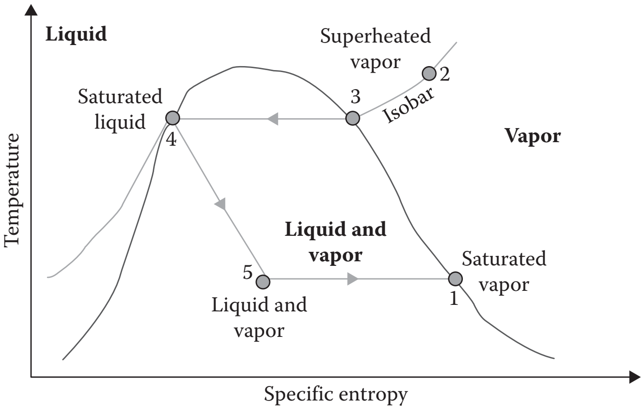

FIGURE 1.2
Temperature versus entropy diagram of the vapor-compression cycle.

salt is allowed to absorb heat, the particles' polarity is randomized again. However, this change requires input of energy, which is taken from the material that is being cooled, causing its temperature to drop. This method has been used to produce some of the coldest temperatures that have ever been achieved, effectively, within a few thousandths of a Kelvin from absolute zero. A related phenomenon is nuclear demagnetization, which involves the magnetization and demagnetization of atomic nuclei. This method has been successfully used to lower temperatures of systems to within a few millionths of a degree from absolute zero; however, temperatures within a few billionths of a degree above absolute zero have also been achieved, although these temperatures are only those of the nuclei, which are not in equilibrium with the warmer electrons or lattice.

1.5 Applications

The applications of low temperatures were conceived of, and applied by, physicists, chemists, materials scientists, and biologists who study the properties of metals, insulators, semiconductors, plastics, composites, and living tissue [Weisend, 1998; White and Meeson, 2002; Pobell, 2007]. Once it became possible to reach temperatures approaching absolute zero, many discoveries and related applications emerged. Generally, the use of cryogenic temperatures offers many benefits, which can be sorted into seven categories: (1) long-term preservation of biological material and food; (2) densification (liquefaction and separation of gases); (3) creation of macroscopic quantum phenomena (superconductivity and superfluidity); (4) reduced thermal noise; (5) low vapor pressures (cryopumping); (6) temporary or permanent property changes; and (7) tissue destruction (cryoablation). Applications of cryogenics usually make use of one or more of these benefits. To be useful, the benefit must be significant enough to warrant the extra effort to reach cryogenic temperatures.

Earlier, superconductivity and its application for levitation were mentioned [Seeber, 1998]. Another important cryogenic property is the fact that many materials become brittle at extremely low temperatures. This property is used by the recycling industry, where recyclables are immersed in liquid nitrogen, making them easy to pulverize and separate for reprocessing. Also, the fact that materials contract at low temperatures is used in the manufacture of automobile engines, where tight-fit applications are made by shrinking components and inserting them into the required cavity. Once expanded at room temperature, a part with a very tight fit is produced.

Cryogenic liquids, including rocket fuel and coolants, are widely used in the various programs of international space agencies. Typically, for rockets, a pair of tanks is used, where one is filled with liquid hydrogen as the fuel that is burned and the second one is filled with liquid oxygen used for the combustion. Elsewhere, liquid helium is used for space applications to cool orbiting infrared telescopes that are designed to detect objects that emit heat; they need to be cooled in order to prevent the instrumentation from being blinded to the infrared radiation from stars by its own emitted heat (Chapters 6 and 9). Since the temperature of superfluid liquid helium is 1.8 K, the telescope can easily pick up infrared stellar radiation with temperatures that are as high as about 3 K.

Cryogenic liquids such as oxygen, nitrogen, and argon are often used in industrial and medical applications (Chapter 11). An example of the use of liquid nitrogen for testing thermal insulation systems is shown in Figure 1.3 [Augustynowicz et al., 1999]. This application is used to provide energy conservation and involves establishing a cold boundary temperature as well as providing a direct measure of the heat flow. This includes fast freezing of some foods for prolonged preservation. The fact that the electrical resistance of most metals decreases as the temperature decreases is used in hospitals for the magnets in magnetic resonance imaging (MRI) systems. Electromagnetic coils with wires that are made of niobium alloys are cooled to 4.2 K and produce extremely high magnetic fields with no generation of heat and no consumption of electric power.

Other medical applications of cryogenic temperatures include the freezing of portions of the body to destroy tissues, a process known as cryosurgery. This process is used to treat cancers and abnormalities of the skin, cervix, uterus, prostate gland, and liver as well as surficial warts. Also, cryogenic temperatures are used for freezing and preserving biological materials including livestock semen as well as human blood, tissue, and embryos. Moreover, there is a practice of freezing the entire human body after death in the hope of restoring the life of the person at a later time. This practice, known as cryonics, is, however, not an accepted scientific application.

FIGURE 1.3
Liquid nitrogen is used in testing of thermal insulation systems for both establishing a cold boundary temperature and providing a direct measure of the heat flow. (Photo courtesy of James E. Fesmire/NASA-KSC.)

1.6 Summary

The range of temperatures that are called cryogenic is from as high as –150°C (–238°F) to absolute zero (–273°C or –460°F), where the latter is the theoretical level at which matter is at its lowest energy, or ground, state. In the absolute, or Kelvin, scale, this lowest temperature is written as 0 K (without a degree sign). Generally, these are extreme conditions at which the properties of materials such as strength, thermal conductivity, ductility, and electrical resistance are altered. Various methods are used to reach cryogenic temperatures and, as described in this chapter, these methods are based on heat conduction, evaporative cooling, cooling by rapid expansion, and adiabatic demagnetization. The tools that allow materials to reach cryogenic temperatures are called cryocoolers and are mostly based on heat exchange, as described in Section 1.4. Applications of cryogenic temperatures involve such fields as physics, chemistry, materials science, and biology. Further details about the applications and effects of such low temperatures are discussed in this book.

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Cryocooler—http://en.wikipedia.org/wiki/Cryocooler

Cryogenic Society of America, Cold Facts Newsletter—www.cryogenicsociety.org

Superconductivity—http://www.superconductors.org/Uses.htm; http://www.superconductors.org/index.htm

The Basic Refrigeration Cycle—http://www.achrnews.com/articles/the-basic-refrigeration-cycle

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