

Low Temperature Materials and Mechanisms



edited by
Yoseph Bar-Cohen



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Preface

Operating at cold temperatures is essential to many science and engineering processes including refrigeration, space exploration, electronics, physics, chemistry, thermodynamics, and medicine. For thousands of years, humans have used temperatures near the freezing point of water and taken advantage of the resulting benefits. Over the last two centuries, it has become feasible to reach cryogenic temperatures as a result of the development of effective coolers. The production of cryogenic temperatures involves several challenges and disadvantages and, to be useful or marketable, applications need to have benefits that outweigh the disadvantages.

Generally, cryogenics is the science and engineering of creating and investigating low-temperature conditions. 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 and were named permanent gases. These gases were carbon monoxide, hydrogen, methane, nitric oxide, nitrogen, and oxygen, with the most attention given to the primary constituents of air—oxygen and nitrogen. While 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, and today the definition refers to temperatures below approximately -150°C (-238°F). In 1894, Kamerlingh Onnes, of the University of Leiden, 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. 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. 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. In 1898, the liquefaction of hydrogen was successfully accomplished by the Scottish chemist James Dewar. In 1908, the last remaining gas element, helium, was successfully liquefied at 4.2 K by the Nobel laureate Dutch physicist Heike Kamerlingh Onnes.

Increasingly, 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 the 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, organs, and embryos. Furthermore, cooling is used to increase electrical conductivity, leading to superconductors that enable such applications as levitation, highly efficient electromagnets, etc. The subject of low temperature materials and mechanisms is multidisciplinary and includes chemistry, material science, electrical engineering, mechanical engineering, metallurgy, and physics.

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.

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. A gas with 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 and energy 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.

The measurement of cryogenic temperatures requires methods that are not commonly used in daily life, which are mostly based on the use of mercury or alcohol thermometers, since 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 by calibration against the primary ones and they are based on measuring physical variable changes for which the response is determined theoretically.

Chapter 1 of this book provides an introduction to the physical parameters, methods of generating cryogenic temperatures, the measurement of temperature, and applications of low temperatures. The other chapters of this book cover some of the key aspects of the field including chemistry and thermodynamics (Chapter 2); materials science of solids and fluids (Chapter 3); characterization methods (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); and applications to the field of physics (Chapter 13), as well other applications and the challenges in 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).

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1

Introduction to Low Temperature Materials and Mechanisms

Yoseph Bar-Cohen and Ray Radebaugh

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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 Rethwisch, 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	$^{\circ}\text{C}$	$^{\circ}\text{F}$
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 through 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

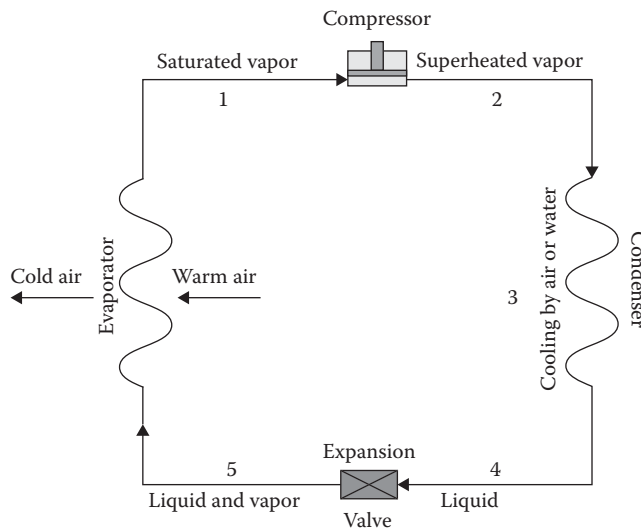


FIGURE 1.1
Typical vapor-compression refrigeration.

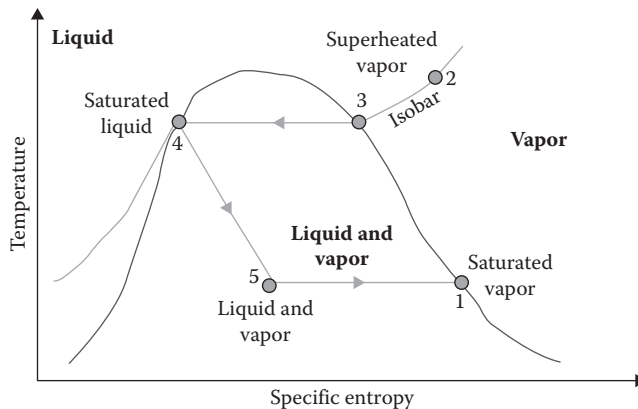


FIGURE 1.2
Temperature versus entropy diagram of the vapor-compression cycle.

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.

Acknowledgments

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Internet Links

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- 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>
- Wikipedia: Carnot Cycle—http://en.wikipedia.org/wiki/Carnot_cycle#The_temperature-entropy_diagram



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2

Chemistry, Thermodynamics, and Material Processes at Low Temperatures

Murthy Gudipati

CONTENTS

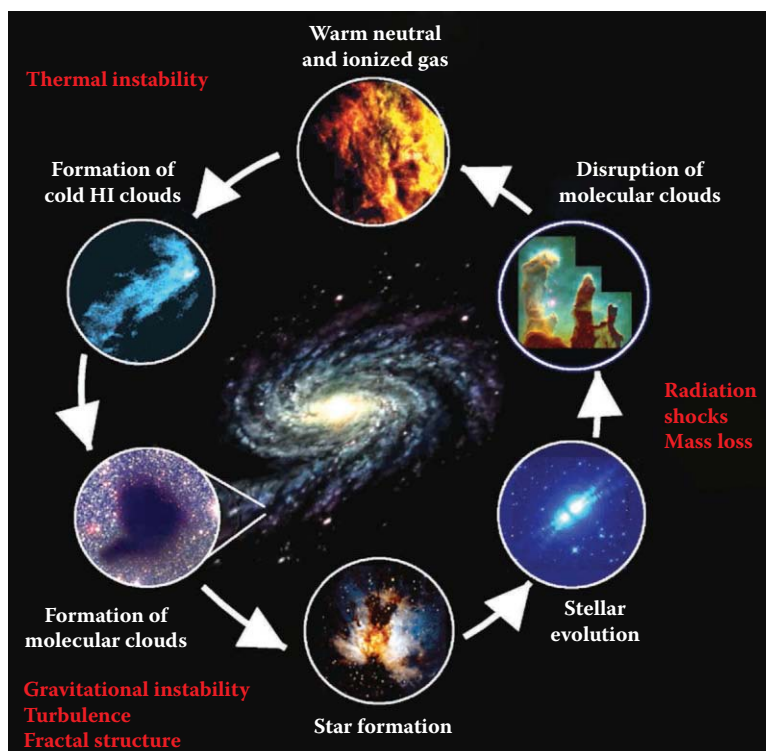
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2.1 Introduction

This overview of low temperature materials in the universe is by no means exhaustive or unbiased. However, it is intended to give the reader a quick glance into the low temperature materials present in space, what we know, and what we still need to understand.

When we speak about cryogenic temperatures, we would like to define the temperature as the meaning varies for different communities. The general definition is unconstrained—very low temperature. For the purposes of this section, we will use the cosmic microwave background (CMB) thermal radiation at 2.72548 K [Fixsen 2009] as the lowest limit and the crystalline water-ice sublimation temperature at ~160 K as the higher temperature limit. This range covers a wide variety of bodies in the solar system and beyond into the interstellar medium. Although sub-Kelvin temperatures are reached in laboratories on Earth, their relevance to astrophysics and planetary sciences (space conditions in general) is not immediately evident.

Our sun is one of the few billion stars in our galaxy and our Milky Way galaxy is one among the several billion galaxies in the universe that are visible both to the naked eye and to instruments in our possession such as space telescopes. Recent developments in exoplanet research increased the potential for the existence of habitable solar systems like ours in our galaxy [Kerr 2013; Schilling 2007; Schwarzschild 2014]. Thus, understanding materials in our solar system that occur under cryogenic conditions would help in understanding many other such solar systems as well as the interstellar medium.

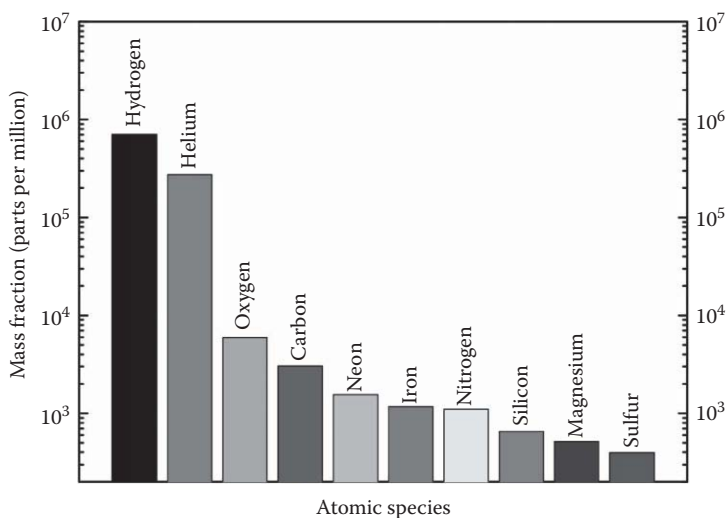
**FIGURE 2.1**

The birth and death cycle of solar systems and the role of interstellar medium in transporting the cryogenic materials in this cycle. Except for the closer vicinity of stars, star-forming regions, and protoplanetary disks, the remainder of the material is typically under cryogenic temperatures. (From <http://sora.as.arizona.edu/HEAT/science/LifeCycle.png>.)

The birth and death cycle of solar systems like ours, and the role of the interstellar medium in the evolution of the cryogenic materials in this cycle [van der Tak 2012], are shown in Figure 2.1. Most of the galaxies or the solar systems in them are at cryogenic temperatures. Away from a star or a protostar (a star in birth), radiation flux per unit area falls by the inverse-square of the distance from the star, resulting in cryogenic temperatures at farther distances where most of the volatiles condense, forming a part of the outer solar system and interstellar matter. This makes understanding of material properties in cryogenic temperatures an important aspect of space sciences, particularly astrophysics and planetary sciences. This chapter reviews the physical, chemical, and material processes at cryogenic temperatures pertinent to the two aforementioned areas of research.

2.2 Material in the Solar System and Interstellar Medium at Very Low Temperatures

The cosmic abundances of elements [Arnett 1996] are shown as a bar graph in Figure 2.2. Hydrogen (H) is the most abundant element, followed by helium (He), oxygen (O), carbon (C), nitrogen (N), etc., and molecules formed by these elements, such as H_2 , O_2 , H_2O , CO,

**FIGURE 2.2**

The abundances of the most predominant elements [Arnett 1996] in our solar system, which are somewhat similar to the galactic abundance. While helium (He) and neon (Ne) are inert elements and cryogenic liquids, the rest of the elements form the basis of a wide variety of molecules in the universe.

N_2 , NO, NH_3 , etc., are the key determiners of cosmic cryogenic chemical composition. While H_2 exists as a liquid and a solid at very low temperatures, He needs even lower temperatures to reach the liquid phase, and only when doped with impurities under special conditions can solid He be made in the laboratory [Kim and Chan 2012; Pratt et al. 2011]. Solid *para*- H_2 [Fajardo and Tam 1998; Momose and Shida 1998] is used as a quantum solid to study the spectroscopy of trapped atoms and molecules at temperatures typically below 5 K. In space, liquid hydrogen is proposed to exist at extremely high pressures and temperatures at the cores of giant gas planets Jupiter and Saturn [Saumon and Guillot 2004; Trachenko et al. 2014], but not as a liquid or solid at low temperatures.

Thus, low temperature environments in the universe can be approximated as locations distant from any star (or star-forming region), taking our Sun as an example. A temperature versus distance plot of our solar system and a protostar (a star in the formation) is shown in Figure 2.3. It is generally accepted that water-ice formation is the starting point of the low temperature front (also known as the snow-line), assumed to be around 100 K [van Dishoeck 2014] in astronomical time and extremely high vacuum ($\sim 10^{-20}$ mbar or a few molecules per m^3), for ice to sublime to water vapor compared to ~ 160 K in the laboratory.

After molecular hydrogen (H_2), by far the most abundant molecules are CO and water (H_2O) in interstellar space [Aikawa et al. 1999], which can also be easily inferred from the cosmic abundance of elements shown in Figure 2.2. Other molecules with significant abundances include CO_2 , C_2H_6 , NH_3 , SO_2 , CH_3OH , etc., all of which are seen both in interstellar ice grains [Gibb et al. 2004; Oberg et al. 2011] and in comet outgassing [Bockelee-Morvan et al. 2000; de Val-Borro et al. 2013]. Under pressure, water becomes a solid at noncryogenic temperature, as exemplified by the formation of ice on Earth, but most of the solar system bodies without atmosphere and the medium between stars (interstellar medium) have water-dominated ice either on the surface or near subsurface. Thus, in the context of space sciences, ice becomes the first target of a solid at cryogenic temperatures. CO, N_2 , and CH_4 form ice at temperatures below 35 K, making them abundant only on interstellar ice grains

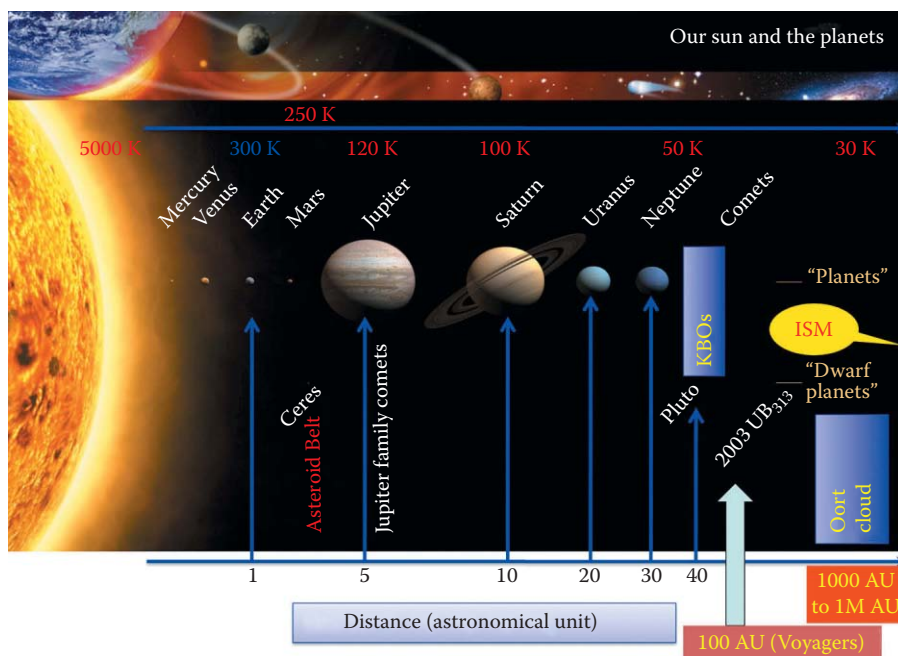
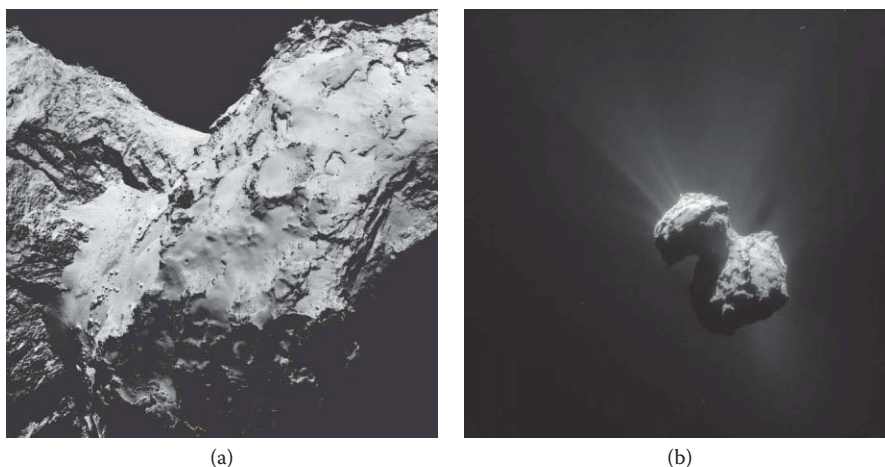


FIGURE 2.3

Temperature versus distance plot of our solar system and potentially other habitable protostars (a star in the formation phase). The Kuiper Belt and Oort cloud contain reservoirs of comets, but comets have eccentric orbits that vary significantly. Material exists under cryogenic temperatures at farther distances from the Sun (several astronomical units—AU—the distance between the Sun and the Earth) and in completely shadowed (from sunlight) surfaces of poor thermal conductivity and no atmosphere, such as on the permanently shadowed regions of the Moon, comets, and asteroids. (Photo courtesy of NASA/JPL [modified].)

(~10 K) and outer solar system icy bodies (beyond Neptune—trans-Neptunian objects or TNOs; Kuiper Belt objects [KBOs], including Pluto), and in the Oort cloud. Comets originate from KBOs and the Oort cloud. A recent book co-edited by the author gives a comprehensive overview of the cryogenic ices in the solar system [Gudipati and Castillo-Rogez 2013], and a review by Clark et al. [2014] provides more details on cryogenic materials in space. KBO comets are scattered into the inner solar system and form so-called short-period comets, whose aphelion is closer to Jupiter's orbit. The interior temperature of a comet is expected to be <50 K, and the comet interior contains these volatile hydrocarbons, as evident from outgassing from comets (comet tails) during a comet's approach closer to the Sun in its eccentric orbit. At the time of this writing, the Rosetta spacecraft is in a close encounter with comet 67P/Churyumov-Gerasimenko (Figure 2.4) studying its surface, interior, coma, and tail composition. Due to the extreme temperature changes a comet undergoes during its eccentric orbits around the Sun and due to the fact that the density of a comet is $\sim 470 \pm 45 \text{ kg/m}^3$ [Sierks et al. 2015], making 70% of its volume porous voids, cometary material composition and its physical properties are still a puzzle. Prior to the Philae lander's deployment, it was expected that comets were loosely bound materials with very low tensile strength and high porosity. Because of this, the consensus was that any attempt to land on a comet should be exercised carefully in order not to get sunk into this low-tensile material. However, the Philae lander unexpectedly bounced several times before landing on comet CG/67P, indicating that the surface was much harder than would be expected from a fluffy low-tensile ice/mineral/organic mix [Faber et al. 2015].

**FIGURE 2.4**

The Rosetta spacecraft is presently in a close encounter with comet 67P/Churyumov-Gerasimenko (CG/67P). (a) Irregular shape of the comet with smooth and rugged terrain. (b) Jets of water, carbon dioxide, and other volatiles coming out of the comet from the sunlit surface. (Photo courtesy of ESA/NASA/JPL.)

KBOs contain Pluto and even bigger icy objects such as Eris, Makemake, Haumea, etc., which have been shown to have methane ice on the surface [Schaller and Brown 2007]. Traveling from KBOs toward the Sun, we encounter Neptunian, Uranian, Saturnian, and Jovian systems. Icy bodies in these systems are observed to consist of mostly crystalline water-ice surface [Fraser and Brown 2010; Grundy et al. 2006]. Table 2.1, compiled from data

TABLE 2.1

The Leading Composition of the Surfaces of Objects That Are at Cryogenic Temperatures and Covered with Various Forms of Frozen Molecular Ices

Distance from the Sun (AU)	Object	Surface Ice Composition
1	Earth	H ₂ O
1.5	Mars	H ₂ O, CO ₂
5	Jovian System	
	Io	SO ₂ ,
	Europa	H ₂ O, Salts
	Ganymede	H ₂ O
	Callisto	H ₂ O
10	Saturnian System	
	Mimas, Enceladus, Tethys, Dione, Rhea, Hyperion, Pohebe, Rings	H ₂ O
	Iapetus	H ₂ O, CO ₂ , Hydrocarbons
20	Uranian System	
	Ariel, Umbriel	H ₂ O
	Miranda	H ₂ O, NH ₃
	Titania, Oberon	H ₂ O, Hydrocarbons
30	Neptunian System	
	Triton	N ₂ , CH ₄ , CO, CO ₂ , H ₂ O
40	Kuiper Belt Objects (KBOs)	
	Pluto, Eris, Makemake, etc.	N ₂ , CH ₄ , CO, H ₂ O

Source: Compiled from Roush, T. L., *Journal of Geophysical Research Planets*, 106, 33315–33323, 2001.

published by Roush [2001], gives a quick overview of major surface composition of objects that are at cryogenic temperatures and covered with various forms of frozen molecular ices. Excellent review articles by Clark et al. [2013] and de Bergh et al. [2013] give detailed data about icy cryogenic surfaces in the outer solar system. Except for Io (dominated by sulfur) and Titan (dominated by hydrocarbons), most of the solar system icy objects are covered with water-ice, and as the surface temperatures become cold enough, N_2 and CH_4 ice are formed on objects such as Pluto and Triton [Cruikshank 2005; Stern 2015]. The Jovian moon Io has a mean surface temperature of ~ 110 K with sulfur-dominated cryovolcanism. Titan, the largest moon of Saturn, is one of the three bodies with significant atmosphere (Venus, Earth, and Titan) in our solar system. With its surface temperature of ~ 94 K and about 1.5 bar surface pressure, Titan's surface harbors liquid hydrocarbon lakes as well as a solid hydrocarbon surface (Figure 2.5).

At even closer distances, Mars has polar H_2O and CO_2 ice, which sublime and recondense with seasonal variations [Kieffer et al. 2006] with temperatures reaching as low as ~ 120 K (Figure 2.6). Finally, the Moon, the closest object to Earth, has on its surface the coldest temperature on its permanently shadowed crater surface (~ 30 K) [Colaprete et al. 2010; Lanzerotti et al. 1981] and can potentially harbor a significant amount of water that can be utilized for future human explorations to the Moon.

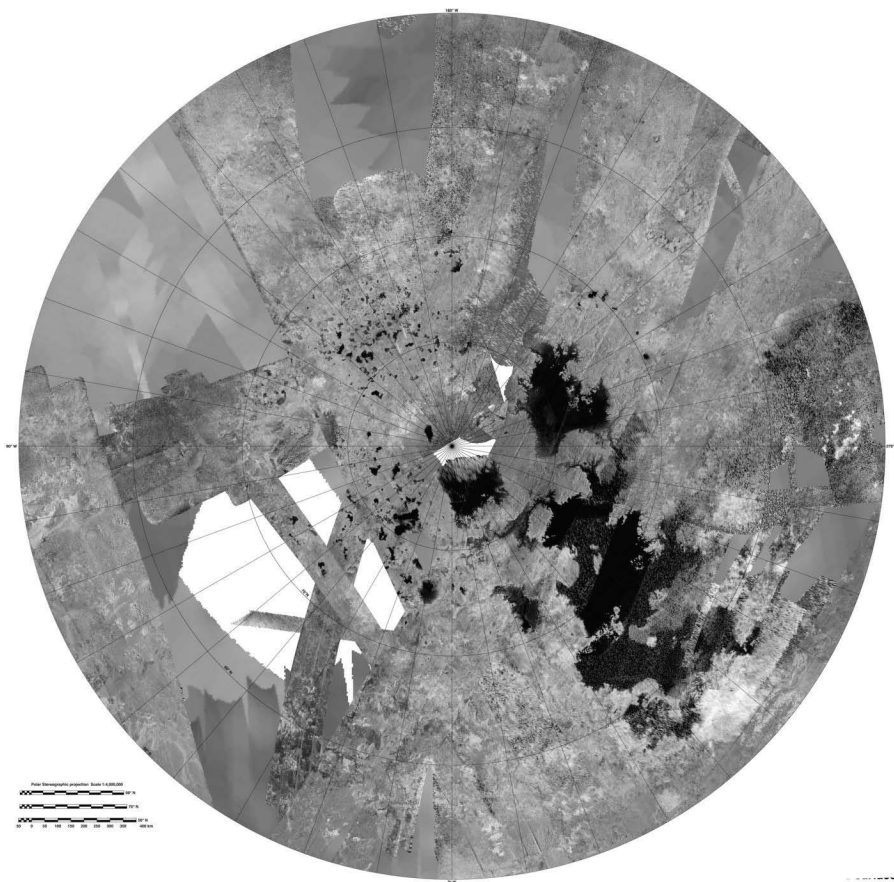
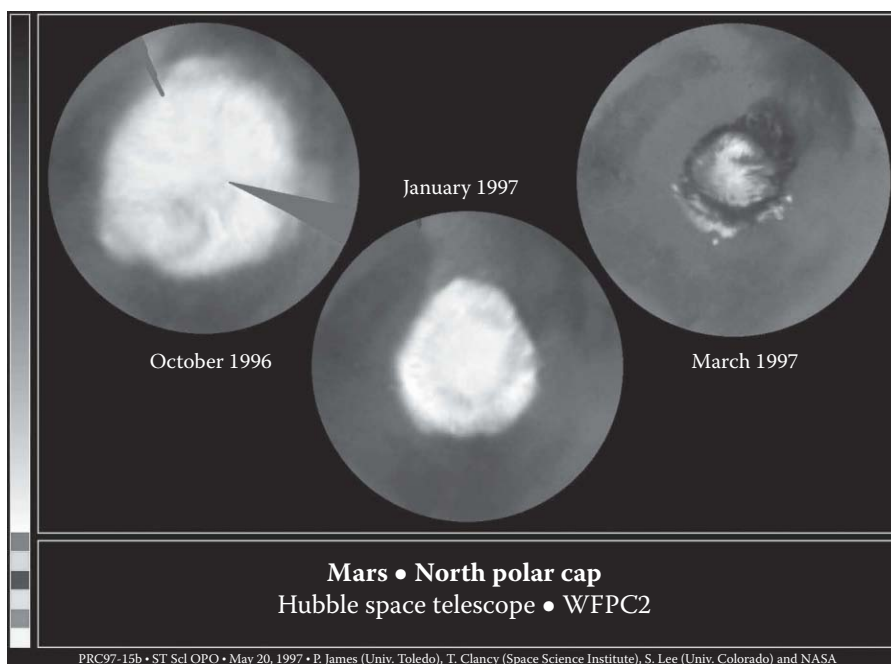


FIGURE 2.5

Cassini mission rendered radar surface mapping of Titan, revealing that Titan's surface harbors liquid hydrocarbon lakes as well as solid hydrocarbon surface. (Photo courtesy of NASA/JPL.)

**FIGURE 2.6**

Northern polar cap images of Mars taken at different seasons from the Hubble Space Telescope (HST). Snow and a warm-up cycle can clearly be seen between winter 1996 and summer 1997. When the surface temperature reaches ~ 150 K, only water snow covers the surface. At lower temperatures (~ 120 K), carbon dioxide condenses, forming a CO_2 ice layer on the top. (Photo courtesy of NASA/JPL.)

This section shows that most of the accessible (for robotic and human reach) low temperature objects in our solar system exist at temperatures at and above 30 K, mostly in solid form, except for the liquid hydrocarbon lakes on Titan. Further, minerals and soil on the Moon, Mars, comets, asteroids, and other objects in the solar system can reach similar extremely low temperatures as their frozen volatile ice counterparts. Understanding their physical and chemical properties under radiation, to be discussed in the next section, is an important and critical component of solar system exploration, as robotic or human missions to these objects need to intimately interact with these objects and their surroundings.

2.3 Energy Sources for the Transformation of Low Temperature Materials (Interstellar versus Planetary)

Energy in the form of electromagnetic radiation (photons) and accelerated particles (electrons, ions, subnuclear particles, etc.) form the basis of the radiation environment in the universe as we know it today. The most commonly encountered radiation in our solar system is in the form of photons from the Sun, solar wind (electrons and ions), and cosmic rays (ions). The energy content of this radiation can span anywhere between 10^{20} eV (galactic cosmic rays) to 10^{-10} eV (long wave ~ 1000 m), as depicted in Figure 2.7. This radiation, constantly impinging on various solar system and interstellar low temperature objects,

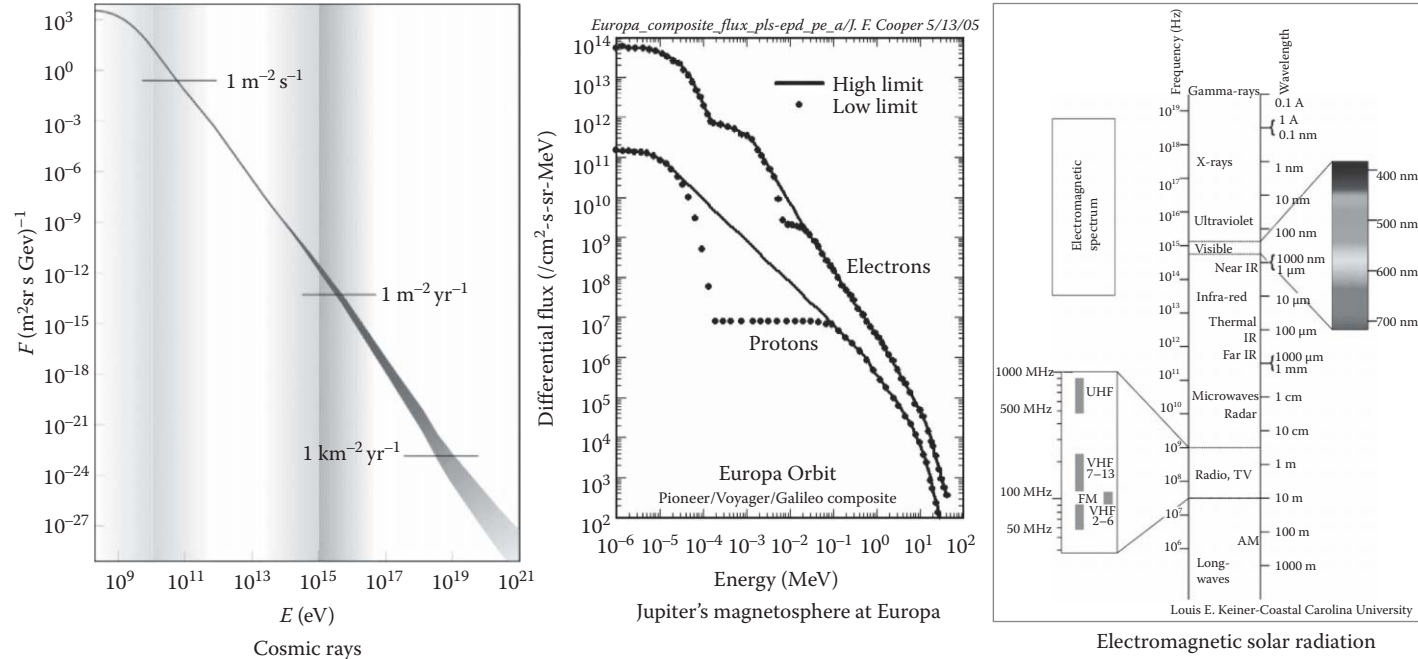


FIGURE 2.7

The energy content of radiation in the universe can span anywhere between $\sim 10^{20}$ eV (galactic cosmic rays) to $\sim 10^{-10}$ eV (long wave ~ 1000 m). The higher the energy content, the deeper it penetrates through planetary surfaces. An analysis of energy content and flux during radiation processing of surfaces of cryogenic solar system bodies is critical for material integrity. (Parts taken from Wikipedia, with permission, and from *Icarus* 149(1), Cooper, J. F., Johnson, R. E., et al., Energetic ion and electron irradiation of the icy galilean satellites, Copyright 2001, with permission from Elsevier.)

causes physical and chemical changes in these materials, some of which are critical for life on Earth (such as photosynthesis). It is generally accepted that energy is one of the four essential necessities for life (water, organics, minerals, and energy). However, the same energy in large doses could also destroy life. Cryogenic temperatures are not expected to be conducive for life, but pockets of warm liquid reservoirs, such as expected under the subsurface of Europa [Khurana et al. 1998; Pappalardo et al. 1999; Schmidt et al. 2011], could be habitable.

2.4 Physical Properties of Water-Ice at Low Temperatures

With water being the dominant molecule on many surfaces, and minerals being present in the form of either dust grains or rocks with little change in their physical properties at lower temperatures, we focus on the physical properties of water-ice in this section. Water-ice on Earth exists in the atmosphere (cirrus clouds), in polar regions as ice caps, and at higher latitudes and elevations (mountains) as snow and glaciers. It exists as very fluffy soft material (fresh snow) and very hard material (ice sheets and ice cores) formed at higher pressures (such as deep beneath the surface). However, most of the ice we find on Earth is not cold enough to be representative of ice on other solar system bodies. For example, ice on Mars reaches temperatures close to 120 K, Jovian icy moons reach similar temperatures, Saturnian moons reach ~ 100 K, and so on. Cometary ice is expected to be ~ 30 K in the interior, with extremely high porosity (close to 70%), but it is still a puzzle whether the cometary interior is made of amorphous or crystalline ice. Thermal properties of ice have an important influence on the physical and chemical transformations within these ices. Thermal properties of loosely bound highly porous materials with large voids are known to be drastically different from strongly bound low-porosity materials. An example of such highly porous materials is aerogel [Kwon et al. 2000]. A few laboratory studies have been attempted for amorphous water-ice and its thermal conductivity as well as porosity comes close to aerogels, of the order of a few $\text{mW m}^{-1} \text{K}^{-1}$. However, literature values for amorphous ices at low temperatures and low pressures vary by about three to four orders of magnitude ranging between 200 and $0.01 \text{ mW m}^{-1} \text{K}^{-1}$ [Bar-Nun and Laufer 2003; Klinger 1980; Kouchi et al. 1992], indicating the need for further accurate experimental work.

Tensile strengths of low temperature ices are also important for in situ lander missions to these bodies, as demonstrated by the recent Philae landing. Typically, tensile strength decreases with high porosity, similar to the decrease in the thermal conductivity. Powders of cryogenic ices and organics should have lower tensile strengths compared with the crystalline ice blocks. Here again, there is a need for more laboratory work. One of the few available studies on the tensile strength of amorphous ice gives a value of $\sim 10^3$ – 10^5 dynes cm^{-2} [Bar-Nun and Laufer 2003; Greenberg et al. 1995], several orders below the tensile strength of crystalline ice, found to be $\sim 10^7$ dynes cm^{-2} [Petrovic 2003]. The Philae lander of the Rosetta spacecraft found that the surface of the comet CG/67P is much harder than expected [Faber et al. 2015; Hand 2014], which caused it to bounce a few times before finally ending in a rugged, shadowed part of the comet (Figure 2.8). A recent laboratory study [Lignell and Gudipati 2015] indicated that when amorphous ice at higher temperatures converts into harder crystalline ice, organic molecules are expelled—simulating the observations made by the Rosetta VIRTIS instrument [Capaccioni et al. 2015].

Other physical properties include heat capacity, bulk modulus, shear and compressive strength, speed of sound, hardness, viscosity, density, etc. While H_2O ice still needs to be

**FIGURE 2.8**

A photograph taken by the Philae lander (Rosetta mission) in a shaded region on comet 67P/Churyumov-Gerasimenko. (Photo courtesy of ESA/NASA/JPL.)

adequately studied for all its aforementioned physical properties, other ices in the solar system such as N_2 , CH_4 , SO_2 , CO_2 , etc., and mixtures of these ices with mineral grains and organic polymers (such as seen on cometary surfaces and on Iapetus) are also poorly studied. Thus, there is a critical need to study the cryogenic physical properties of a wide variety of molecular ices at macroscopic and microscopic levels.

Extremely low temperatures also pose challenges for materials that can be used for various missions. While many parts of the spacecraft or lander can be protected from cryogenic temperatures through thermal packaging, some parts that interact with the bodies such as drills, anchors, optical equipment for subsurface in situ observations, etc., must be in a position to operate effectively at that temperature, making their fabrication at room temperature extremely difficult. For example, a comet subsurface cryogenic sample analysis (return) mission should have all the exposed parts cryogenically qualified to a minimum of 50 K. Ideally materials for such an application must have the lowest possible thermal expansion or contraction coefficients, no changes in their tensile strengths and brittleness, etc. While the mechanical parts need to retain their functional and material integrity at extremely low temperatures, these and other parts of the spacecraft must also retain their chemical integrity under low temperature and high-radiation conditions such as on Europa, one of the Galilean moons of Jupiter.

2.5 Chemistry at Cryogenic Temperatures

Chemical processes at temperatures below 160 K are mostly caused by radiation (Figure 2.7) that supplies the necessary energy to overcome reaction barriers, barrierless chemical reactions, and light-atom (typically hydrogen) tunneling. While the first two categories dominate a majority of chemical processes in the solar system, tunneling becomes important at extremely low temperatures (<30 K) and over long periods of time [Arnaut et al. 2006; Goumans 2011; Goumans and Andersson 2010]—both appropriate for interstellar conditions. In general, chemical reactions at low temperatures occur at a lower rate than reactions at higher temperatures, mainly due to (thermal) reaction barriers that become larger than the ambient thermal energy available as the temperature lowers [Cavalli et al. 2014]. In general, lower temperatures lower the molecular mobility (including rotations

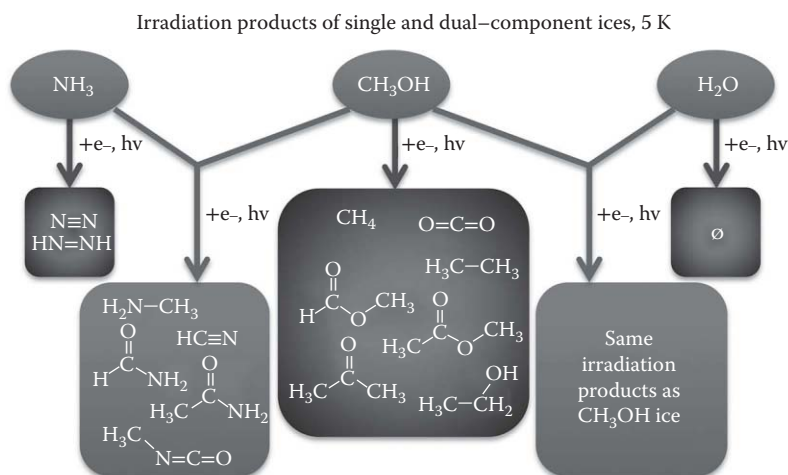
and diffusion), slowing or stopping bimolecular reactions and diffusion-controlled chemical pathways. However, radiation-induced monomolecular chemistry such as molecular dissociation and ionization as well as barrierless reactions will continue to be dominant even at very low temperatures. Our recent work, utilizing newly developed techniques to look at the composition of cryogenic materials using laser ablation and laser ionization time-of-flight mass spectrometry, showed that indeed ionization and other radiation-induced chemistry resulting in complex prebiotic organic molecules could occur even at 10 K—a temperature predominant in the dense molecular clouds (DMSs) of the interstellar medium [Gudipati and Yang 2012; Henderson and Gudipati 2015]. At higher temperatures (such as the solar system temperature >30 K), the radiation-induced chemical processes become even more important. This applies to both the solar system body and the spacecraft parts that are exposed to radiation. Chemical integrity at low temperatures is critical for the functioning of many spacecraft parts. These processes must be taken into account when developing new spacecraft shields or shieldless low-mass CubeSat-like spacecraft.

2.6 Evolution of Complex Molecules in the Coldest Places in the Universe

Atoms and molecules in space (Figure 2.2 and Table 2.1) are constantly subjected to radiation and thermal processing. Whether considering minerals such as silicates, organics such as the polycyclic aromatic hydrocarbons (PAHs) that seem to be abundant in the universe, or other molecular materials that form the basis of surfaces on solar system objects, all these materials are subjected to chemical processing. For example, radiation can cause photoionization (ejection of an electron from the molecule or material), resulting in the formation of an electron–hole pair. This charge separation can initiate a wide variety of chemical evolution processes such as charge-mediated chemistry, Coulomb force–driven long-range effects on the surface, photocurrents, etc. This can equally affect salts such as MgSO_4 , NaCl , or the corresponding acids expected to be the predominant on Europa’s surface, which is bombarded with radiation and ions [Carlson et al. 2009; Dalton 2003; Hand and Carlson 2015; Hoerst and Brown 2013; Munoz-Iglesias et al. 2014]. Neutral atoms can be ejected into the atmosphere through photo-attachment (electron attachment to ions or molecules) processes. Molecular dissociations (breaking of a covalent bond) also play a key role in ejecting neutral and ionized volatiles into the tenuous atmosphere of airless bodies. On the Moon, solar radiation and cosmic ray-driven production of H, O, and other neutral and charged species (H^+ , O^+ , etc.) forms the basis for its atmosphere. Similar processes occur on Europa, Titan, Ganymede, etc. We found that when water-ice containing organic impurities is subjected to photon or electron irradiation, ionization is the primary process [Gudipati 2004; Gudipati and Allamandola 2004], followed by a wide range of complex chemical processes that could form the basis for the composition of prebiotic materials on Earth (Figure 2.9).

2.7 Kinetic versus Thermodynamic Processes at Very Low Temperatures

Most of the radiation-driven processes are kinetically controlled, resulting in a larger amount of local excessive energy. However, processes that occur at thermodynamic equilibrium play a leading role at astronomical timescale. Such processes include chemical

**FIGURE 2.9**

Complex prebiotic molecules that are detected in the laboratory using in situ laser ablation time-of-flight mass spectrometry from simulated cometary and interstellar ice composition under radiation processing with electrons and UV photons. Boxes show complex organics produced from the initial simple ices and ice mixtures (shown by connecting lines and arrows). Although oxygen species such as O, O₂, H₂O₂, O₃, etc., are produced from pure H₂O ice, their mass spectral signals are strongly overlapped by H₂O signals. Most of the complex organic molecules detected in this laboratory study have also been found on comet tails and ice grains in the interstellar medium [Henderson and Gudipati 2015]. Other ices pertinent to the outer solar system, such as CH₄, CO, N₂, CO₂, SO₂, etc., need to be further studied.

reactions or material phase transitions with a barrier that is comparable with the thermal history of the body [Mastrapa et al. 2013]. Tunneling of a proton (hydrogen) could also lead to chemical reactions at very low temperatures [Hama and Watanabe 2013; Henkel et al. 2014; Herbst 1994]. Kinetically controlled processes include photon-, electron-, or ion (cosmic rays or local magnetospheric radiation)-induced sputtering of the surface [Brown et al. 1986; Johnson et al. 2013], and dust and micrometeorite bombardment [Pham et al. 2009; Turrini et al. 2014]. Penetration depths of such energetic processing are determined by the energy and mass of the particle. Cosmic rays with the highest energies can penetrate several meters below a soil, rock, or ice surface. The rest of the ions, dust, and micrometeorites only affect the first few millimeters of the surface [Cooper et al. 2001].

2.8 Material Properties for Cryogenic Solar System Explorations

Solar system exploration has always pushed the science and engineering capabilities to (and beyond) the limits. In situ explorations to low temperature parts of our solar system pose challenges that not only require material integrity at extremely low temperatures (~30 K), but also must be compatible with very low-sunlight conditions, whether on the permanently shadowed craters of the moon, or Europa's surface, or a comet's shadowed surface. For this reason, many in situ missions at present have very short lifetimes of performance (such as the Philae lander on comet CG/67P), unless local energy sources are available. Future in situ explorations to these extremely cold objects must take these aspects into account: performance under extreme temperature variations, sufficient

hardness to penetrate through surfaces as hard as a rock, energy efficient, lightweight, etc. Long-term (more than a few hours to a day) in situ instrumentation would need even more stringent requirements, especially for high-radiation environments such as on Europa, forcing spacecraft and instrumentation to be high-radiation hard and low temperature stable simultaneously. Radiation-induced chemical degradation of the material surface and interior over a long period of time is expected to be a critical issue for lander missions to bodies without atmosphere (such as asteroids and Jovian satellites like Europa).

2.9 Conclusions and Future Outlook

Solar system explorations, as they expand and reach the extreme corners with extreme temperature and radiation conditions, pose challenging demands for new materials that are thermal and radiation hard, lightweight, high tensile strength, etc. At the same time, understanding the thermal, mechanical, and chemical properties of extremely low temperature solar system bodies—from the permanently shadowed craters of the Moon to comets and KBOs—is equally critical. The next several decades will fill in these knowledge and technology gaps, enabling human and robotic explorations of our solar system.

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3

Solids and Fluids at Low Temperatures

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3.1 Introduction

The fundamental properties of low temperature materials have garnered greater interest with the advent of space exploration. Space technology must survive fluctuations and lows in temperature rarely encountered on Earth. Of deeper scientific interest and continuing mystery is the range of new thermodynamic properties and rheologies (e.g., elasticity, tensile strength, viscosity) of planetary materials encountered on the Moon and Mars, comets, and a multitude of icy worlds. Properties of industrial metals and plastics have been discussed in recent chapters published elsewhere [Van Sciver, 2012], including low temperature heat capacity, thermal contraction, electrical and thermal conductivity, magneto-resistance in metals, and solid–liquid phase changes [Mehling and Cabeza, 2008]. This chapter describes materials and their relevant properties, which we are just beginning to understand in the detail that future exploration requires. It ends with a brief note about applications of piezoelectric materials at low temperatures.

3.2 Solid Materials

At very low temperatures, water and other solid materials that are present on icy satellites have mechanical and chemical properties that resemble those of rocks and metals. This analogy makes them interesting as key to icy satellite geology, but also possibly as industrial materials.

The chemical and physical properties of a solid are greatly influenced by the conditions under which it was formed due to variations in the molecular arrangement. Solids may be *crystalline*, with ordered and repeating fundamental units at the molecular level. This generally gives rise to anisotropic physical properties, higher and sharply defined melting points, and higher thermal conductivities when compared to analog *amorphous* solids that do not have a long-range order [Eucken, 1911; Hendricks and Jefferson, 1933; Lonsdale, 1937]. The degree and type of crystallinity may depend on several factors including pressure, rate and temperature of freezing or deposition, thermal history, specific molecular makeup/existence of impurities, or the presence of bond-disrupting processes [Johannessen et al., 2007; Sestak et al., 2011]. The crystalline state is energetically favored, but kinetically driven formation processes may result in amorphous structures if the atoms do not have time to orderly arrange to the lower-energy crystalline state [Zallen, 1983]. If water is cooled at a rate greater than 10^6 K s^{-1} , the crystalline state does not have time to form and an amorphous solid is formed [Bruggeller and Mayer, 1980].

The geometry of crystalline solids of single repeating units can be classified by one of 14 symmetrically unique lattice structures, called *Bravais lattices*. However, much crystalline material, such as salts or molecular solids, is composed of multiple fundamental units, which break the symmetry of the 14 Bravais lattices and must be defined with additional symmetry elements. These elements are called *point groups*, and the combination of the Bravais lattices and the point groups leads to 230 potential *space groups* that provide the necessary symmetry elements to describe a 3D crystalline solid [Sands, 1975].

Substances often occur in several different crystalline phases—a phenomenon known as *polymorphism*—which depends on the conditions of formation. For example, on distant, frigid bodies of the outer solar system such as Pluto and Triton (a moon of Neptune), nitrogen ice can exist in two phases—a cubic α -phase or a hexagonal β -phase—with a transition temperature between them at 35.6 K. Their differing molecular structures change the electronic and vibrational environment of the material. The difference can be identified in spectroscopic analyses of the surface and has been used to elucidate the surface temperature of these bodies [Grundy et al., 1993; Quirico et al., 1999].

Polymorphism is one of water's anomalous properties: 17 distinct crystalline phases are known at present [Petrenko and Whitworth, 2002; Falenty et al., 2014], labeled by Roman numerals following the chronological order of their discovery. The first new phase (besides hexagonal I_h), described in 1900, was named ice II [Tammann, 1900]; the most recent one, ice XVI, was discovered in 2014 [Falenty et al., 2014]. Other phases may exist [e.g., Wilson et al., 2013; Algara-Siller et al., 2015].

Specific crystal or amorphous structures are identified by analyzing the glass transition temperature or associated thermodynamic quantities; x-ray scattering or electron diffraction patterns; or NMR splitting pattern to determine bond correlation [Stachurski, 2011].

The process of crystallization can be understood as the balance between the enthalpic benefit of bond formation and the entropic drive to disorder. Upon cooling, the kinetic energy of molecules and atoms decreases, diminishing the thermodynamic contribution of entropy. At low temperatures, when the Gibbs free energy is enthalpically dominated,

solidification becomes thermodynamically spontaneous. However, not every thermodynamically favored cooling process immediately results in solidification. Even if the phase transformation of the bulk sample is considered spontaneous, below a critical size the transformation of the molecular units may not be. Nucleation sites, if present, often enable crystal formation by allowing additional transitions to take place [De Yoreo and Vekilov, 2003]. If nucleation sites do not exist, liquids may be cooled below the thermodynamically determined solid-liquid phase boundary—a condition known as *supercooling*. For example, water normally freezes at 273 K at 1 atmosphere of pressure, but can be supercooled at the time scale of milliseconds down to 232 K while remaining liquid [Sellberg, 2014].

3.2.1 Crystalline Ices

The phase diagram shown in Figure 3.1 depicts the stability fields of liquid and solid phases of water. That is, the phase diagram merely shows the one phase that is thermodynamically most stable at a specific combination of pressure P and temperature T . Some ice phases, namely ices IV, IX, XII, XIII, XIV, and XVI, cannot be found in Figure 3.1 because they are never the thermodynamically most stable phase. In spite of this metastable nature, such phases readily form and can be isolated and characterized. They do not convert to more stable ice phases at laboratory time scales, and probably also not at astrophysically relevant time scales, provided the temperature and pressure conditions do not change. Crystalline phases can be stable in a P - T field or metastable at all P - T conditions. Some stable ice phases share a phase boundary with liquid water (ices I_h, III, V, VI [e.g., Choukroun and Grasset, 2007 and references therein] and ice VII [Pistorius et al., 1963; Mishima and Endo, 1978; Datchi

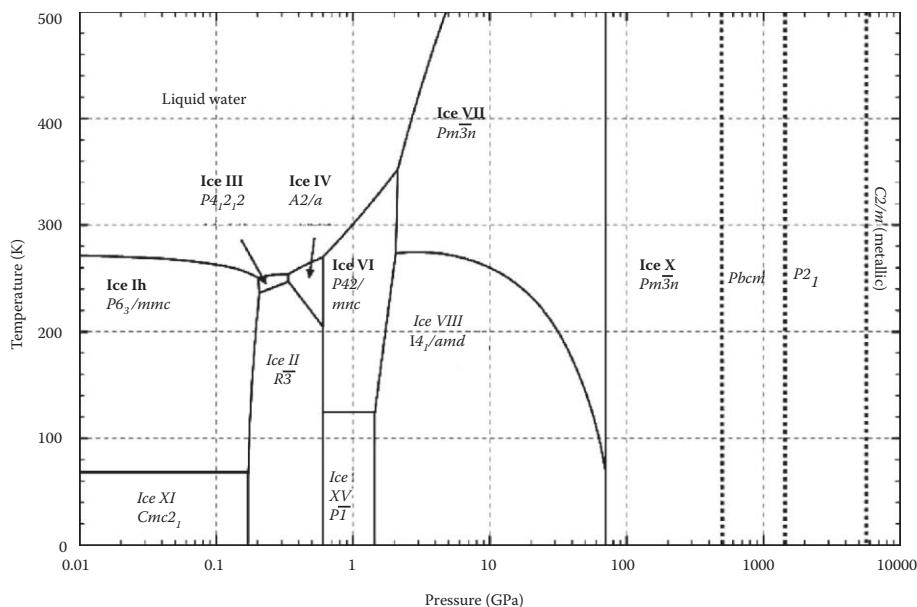


FIGURE 3.1

Phase diagram of H₂O from 0.01 to 10000 GPa and 0 to 500 K, showing stable water phases and their space group when crystalline. Proton disordered phases are written in bold, and proton-ordered phases are written in italics. Phase boundaries are plotted with a thick black line and predicted phase boundaries predicted at ultra-high pressures using computational simulations in dotted lines. (Courtesy of Baptiste Journaux, coauthor of this chapter.)

et al., 2000)), and are disordered [Kuks, 2007]. Other ice phases are proton ordered and only exist in thermodynamic equilibrium with other ice polymorphs, namely ices II [Kamb, 1964; Kamb et al., 1971; Arnold et al., 1968; Fortes et al., 2003, 2005], VIII [Whalley et al., 1966; Kuhset al., 1984; Jorgensen et al., 1984, 1985; Pruzan et al., 1990, 1992; Besson et al., 1994, 1997; Pruzan et al., 2003; Song et al., 2003; Singer et al., 2005; Knight et al., 2006; Yoshimura et al., 2006; Somayazulu et al., 2008; Fan et al., 2010], XI [Singer et al., 2005; Knight et al., 2006; Fan et al., 2010; Tajima et al., 1984; Matsuo et al., 1986; Fukazawa et al., 1998, 2002; Kuo et al., 2005], XII [Kuks et al., 1998; Lobban et al., 2000; Salzmann et al., 2006a, 2006b, 2008; Knight and Singer, 2008], XIV [Salzmann et al., 2006a, 2006b; Tribello et al., 2006], and XV [Kuks et al., 1984; Fan et al., 2010; Knight and Singer, 2005; Kuo and Kuhs, 2006; Salzmann et al., 2009]. Such high-pressure ice phases may be found in the mantles of the icy moons, for example, Ganymede, which is covered by an 800-km-thick layer of water ice [Vance et al., 2014], as well as Callisto [Schubert et al., 2004] and Titan [Tobie et al., 2005; Fortes et al., 2007] (Figure 3.2). It is also expected that high-pressure ices play a key role in ocean planets [Leger et al., 2004; Sotin et al., 2007; Grasset et al., 2009], roughly Earth-sized exoplanets with deep oceans that constitute an interesting analog to the icy satellites (Figure 3.2).

The distinction between proton-ordered and proton-disordered ice phases is shown in Figure 3.3. In all ice phases, the oxygen atoms occupy lattice positions, that is, the oxygen atoms are ordered over long ranges. The hydrogen atoms occupy lattice positions only in

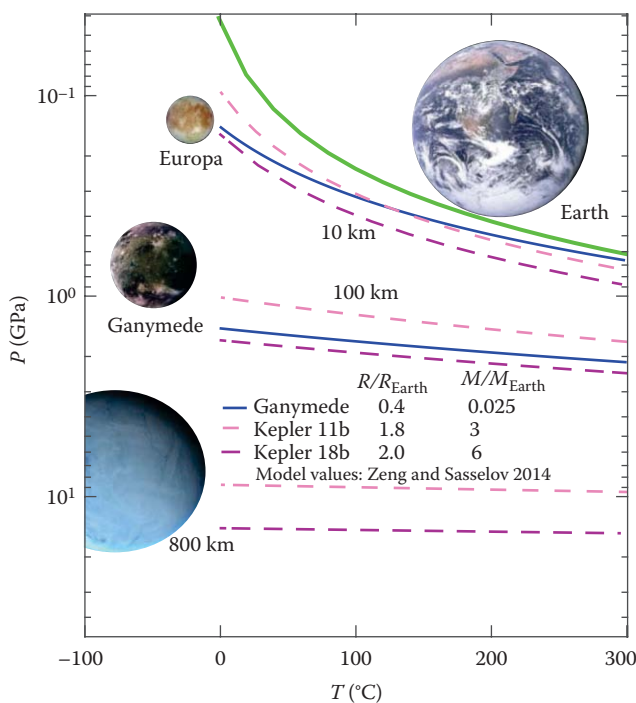
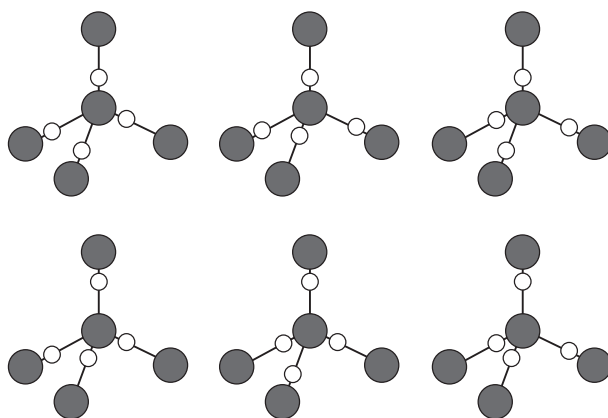


FIGURE 3.2

Pressures in exoplanet oceans span the multi-GPa range of pressures where liquids are possible. A Europa-depth ocean on Earth would behave like Ganymede's ocean in terms of having high-pressure ices. This figure shows profiles of pressure (GPa) and temperature (°C) in the upper mantles of selected objects (modified from Vance, S. et al., *Astrobiology*, 7(6), 2007), beginning at the estimated depth of the seafloor. The overlying ocean is assumed to be at a constant temperature; in general, seafloor temperature will be elevated by more than 40°C in deep oceans. Known exoplanets, albeit very hot ones, are modeled as super Europa objects with seafloor depths like Earth's (10 km), Europa's (100 km), and Ganymede's (800 km). (Courtesy of Steve Vance, principal author of this chapter.)

**FIGURE 3.3**

Six different proton configurations (white circles) allowed by the Bernal-Fowler ice rules. In proton-ordered ices, only one of these is observed, whereas in proton-disordered ices, all of these configurations are observed with equal probability. The tetrahedral coordination around a central oxygen atom (filled circles) is the motif found in all crystalline and amorphous ices (except for the ultrahigh-pressure phases at >100 GPa, ice X and the post-ice X phases). (Adapted from Fuentes-Landete, V., *Proceedings of the International School of Physics "Enrico Fermi," Volume 187: Water: Fundamentals as the Basis for Understanding the Environment and Promoting Technology*, IOS and Bologna: SIF, Amsterdam, 2015.)

the case of the proton-ordered ice phases. For a given network of oxygen atoms, in principle a larger number of ordered proton configurations are possible. Experimentally, however, only a single type of ordering has been observed so far. Ice I_h , the most common form of ice on Earth, is a proton-disordered form of ice. The hydrogen atoms obey the Bernal-Fowler ice rules [Bernal and Fowler, 1933], but they are randomly distributed within the ice crystal. As a result, ice I_h represents a frustrated crystal, which does not have zero configurational entropy at 0 K. The residual entropy at 0 K has become famous as the Pauling entropy ΔS_p [Pauling, 1935] and amounts to approximately $3.41 \text{ J K}^{-1} \text{ mol}^{-1}$. This entropy can be released if one successfully achieves the transformation to the proton-ordered state. The ordered counterpart of ice I_h is known as ice XI, and its possible ferroelectric nature is currently being questioned [Parkkinen et al., 2014]. Order-disorder pairs can be easily recognized in the phase diagram in Figure 3.1 because the pair is separated by a phase boundary parallel to the pressure axis. This is so because there is barely any volume difference between proton-ordered and proton-disordered form, that is, $\Delta V \approx 0$, but the two ices differ by the Pauling entropy, that is, $\Delta S \approx \Delta S_p$. The slope of the phase boundary dP/dT then goes to infinity, that is, parallel to pressure axis, according to the Clausius-Clapeyron equation $dP/dT = \Delta S/\Delta V$.

Solid-solid transitions between polymorphs are possible by either a rearrangement of the O-lattice (density-driven, e.g., by pressurization) or H-ordering/disordering while preserving the geometry of the O-atoms (entropy-driven, e.g., by cooling a disordered phase to form an ordered one). In the case of density-driven transitions, there is a finite volume change ΔV , but the entropy change may be close to zero $\Delta S \approx 0$ if the transition is from a proton-disordered to a proton-disordered phase. Such phase boundaries can be identified easily in Figure 3.1, since they are almost parallel to the temperature axis. With increasing pressure, the transition sequence $I_h \rightarrow \text{III} \rightarrow \text{V} \rightarrow \text{VI} \rightarrow \text{VII} \rightarrow \text{X}$ can be identified. All these ice phases, except for ice X, are proton-disordered and of increasing density, starting at 0.92 g cm^{-3} and ending at 2.50 g cm^{-3} . High density is accommodated by improving packing, bending hydrogen bonds, and forming new hydrogen-network topologies. The oxygen networks differ in terms of topology and ring structure. While ices I_h and I_c consist entirely of six rings, ice V

has 4-, 5-, 6-, 8-, 9-, 10-, and 12-ring structures [Herrero and Ramírez, 2013]. Some structures show ring threading; for example, ice IV and others show two interpenetrating ice networks (self-clathrates), for example, ices VI, VII, VIII, and X. For the latter ultrahigh-pressure ice X (>100 GPa [Benoit et al., 1996; Pruzan et al., 2003]), the molecular nature disappears due to the symmetrization of hydrogen position between the oxygen atoms.

Three low-density variants of crystalline ice can be produced at ambient pressure: hexagonal ice I_h , cubic ice I_c , and ice XI. While ice I_h is the abundant polymorph of solid H_2O on Earth, ice I_c can occasionally be found in clouds [Murray et al., 2005; Mayer and Hallbrucker, 1987; Whalley, 1983]. Ice I_c forms upon heating of amorphous ice in a vacuum or at ambient pressure. It may thus be present on comets after they have experienced temperatures above the crystallization temperature of ~ 150 K. It also forms upon heating of high-pressure forms of ice at/below ambient pressure and upon condensation of water vapor on particles at ~ 140 – 200 K. Both are very similar in density at P_{atm} , also appearing to be identical when probing the short-range molecular environment (e.g., Raman or mid-infrared). However, they can be distinguished when examining the long-range order (e.g., x-ray diffraction or neutron diffraction) [Kuhs et al., 1987]. Ices I_h and I_c are polytypical relative to each other: identical layers—differing stacking order (hexagonal rings, ABCABC with hexagonal symmetry for I_h , ABAB with fcc symmetry for I_c) [Kuhs and Lehmann, 1986; Kuhs et al., 1987; Guinier et al., 1984; Röttger et al., 1994]. I_c is not obtained as a single crystal, but only in the form of small crystallites with roughly hexagonal stacking faults (quantified by “cubicity index”) [Kuhs et al., 1987; Kohl et al., 2000; Hansen et al., 2007]. Ice XI, the proton-ordered form of ice I_h , is only stable at $T < 72$ K. A proton-ordered form of cubic ice I_c might also exist, as has been suggested by *in situ* IR experiments and *ab initio* simulations [Geiger et al., 2014].

As mentioned, a crystalline phase may be transformed into another by ordering/disordering the protons while almost entirely preserving the O-atom topology. These order-disorder pairs will be found in the same P region of the phase diagram (I_h –XI [Singer et al., 2005; Knight et al., 2006; Fan et al., 2010; Tajima et al., 1984; Matsuo et al., 1986; Fukazawa et al., 1998, 2002; Kuo et al., 2005], III–IX [Fan et al., 2010; Kuhs et al., 1998; Lobban et al., 2000; Whalley et al., 1968; LaPlaca et al., 1973; Nishibata and Whalley, 1974; Minceva-Sukarova et al., 1984; Londono et al., 1993; Knight et al., 2006], V–XIII [Kuhs et al., 1998; Lobban et al., 2000; Salzmänn et al., 2006a, 2008; Knight et al., 2008; Martin-Conde et al., 2006; Noya et al., 2008], VI–XV [Kuhs et al., 1984; Fan, 2010; Knight and Singer, 2005; Kuo and Kuhs, 2006; Salzmänn et al., 2009], VII–VIII [Whalley et al., 1966; Kuhs et al., 1984; Jorgensen et al., 1984, 1985; Pruzan et al., 1990, 1992, 2003; Besson et al., 1994, 1997; Song et al., 2003; Singer et al., 2005; Knight et al., 2006; Yoshimura et al., 2006; Somayazulu et al., 2008; Fan et al., 2010], and XII–XIV [Salzmänn et al., 2006a, 2006c; Tribello et al., 2006; Martin-Conde et al., 2006; Noya et al., 2008; Köster et al., 2015]), the ordered phase at lower and the disordered phase at higher temperatures (as the transition connected to the process of disordering an ordered phase is of entropic nature). Six configurations are allowed by the Bernal–Fowler ice rules in the local tetrahedral hydrogen-bond geometry known as Walrafen pentamer. In a fully disordered phase, all six are populated with the same probability (averaged over space/time) [Bernal and Fowler, 1933], whereas in an ordered phase, only one configuration is found. Often, the ordered low temperature phase cannot be accessed due to geometric constraints and kinetic limitations at such low temperatures. Point defects (Bjerrum L/D or ionic defects) in the ice lattice may enhance the reorientational mobility in the ice lattice. By using dopants incorporated into the ice lattice in ice I_h (e.g., HCl, HBr, HF, NH_3 , KOH, etc. [Tajima et al., 1984; Matsuo et al., 1986; Hobbs, 1974; Gross and Svec, 1997]) and also at a higher pressure in ice VII (e.g., NaCl, LiCl, RbI [Frank et al., 2006, 2013; Klotz et al., 2009; Journaux et al., 2015]), such point defects may be introduced deliberately. These extrinsic defects may enhance the mobility

related to rearrangement of protons and/or rotation of H_2O molecules, thereby overcoming kinetic limitations and allowing access to the proton-ordered low temperature phase [Köster et al., 2015]. However, this may also slow down the dynamics. Empirically it has been found that KOH doping accelerates dynamics in ice I_h whereas HCl doping has been found to accelerate the dynamics in the high-pressure ices V, VI, and XII [Salzmann et al., 2006a, 2006b, 2009]. The reasons why one dopant is effective and the other is not are still unclear, but are certainly related to the dynamics of pairs of point defects within the ice lattices [Burton and Oliver 1935; Mayer and Pletzer 1986]. Some ice phases do not form an order–disorder pair; new ice phases related to them through an order–disorder transition may be found in the future. For example, the ordered counterparts of I_c and IV, as well as the disordered one of II, still await discovery [Lokotosh and Malomuzh, 1993; Zabrodsky and Lokotosh, 1993].

The solubility of dopants in ice is generally assumed to be low. Ice I_h tends to reject any impurities during freezing [Gross and Svec, 1997]. For concentrated solutions, for example, freezing aqueous solutions present during sea ice formation, rejected salts may be incorporated in the bulk ice sheet at the grain boundaries as liquid brine inclusions [Weeks and Akley, 1986]. For the H_2O –NaCl system, the partition coefficient K_d (NaCl) is estimated around 2.7×10^{-3} and $3.2 (\pm 0.2) \times 10^{-3}$ [Gross et al., 1977, 1987]. This incompatible behavior of salts in ice I_h has a notable exception with ammonium fluoride, which forms a solid solution by substituting with H_2O molecules up to 5.2 mol% [Gross and Svec, 1997], most likely due to the isomorphism between the crystal lattices of NH_4F and ice I_h . Such incorporation should be distinguished from that occurring in clathrate hydrates as the ice solid solution keeps the crystallographic structure of the pure H_2O phase. While most substances are completely insoluble in ice, some dopants can be incorporated in the ice crystal by replacing water molecules. In cases of HCl, KOH, NH_3 , HBr, or HF, the solubilities are in the ppb and ppm range. In spite of the low solubility, the influence on H-dynamics can be huge.

Recent high-pressure experiments have shown that ice VII can incorporate up to 1.6 mol% of NaCl, 5 mol% of CH_3OH [Frank et al., 2006, 2013], and up to 16.7 mol% of LiCl [Klotz et al., 2009]. Using DFT *ab initio* calculations, Klotz et al. [2009] predict incorporation in ice VII at interstitial (face-centered) and lattice sites (H_2O substitution) for Li^+ and Cl^- , respectively (Figure 3.4). The presence of 16.7 mol% of Li^+ and Cl^- solutes in the ice VII cubic $Pn-3m$ lattice increases the volume of the phase by 8%, increasing the density by 0.2 g cm^{-3} . At low temperatures, the presence of Li and Cl ions inhibits the transition to proton-ordered ice VIII down to 80 K. Strong electrostatic interactions between the incorporated ions and the polar water molecules seem to disadvantage long-range ordering of the H_2O orientations,

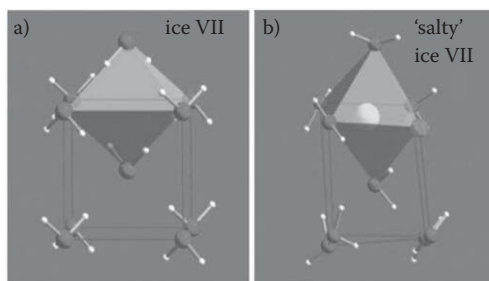


FIGURE 3.4

(a) Proton-disordered ice VII crystallographic structure in one possible proton configuration with the octahedral interstitial face-centered void. (b) Snapshot of a possible configuration of “salty” ice VII ($\text{LiCl} \cdot 6\text{H}_2\text{O}$) derived from *ab initio* calculations illustrating the lattice distortion and H_2O misorientation induced by the incorporation of Li^+ (large circle) and Cl^- (medium circle) ions. (Modified from Klotz, S., *Nat. Mater.*, 8, 2009.)