Chapter 1 Fundamentals of Thermodynamics

This chapter firstly looks back on the development of macroscopic thermodynamics during the last three hundred years and its historical contribution to the social evolvement. The present achievement and challenges are also discussed. To clearly understand the thermodynamic laws, the essential concepts of thermodynamics are defined and clarified. Further, the macroscopic thermodynamics of materials and the fundamental principles of four thermodynamics laws are introduced, which are the essential basis of the later chapters. The intrinsical relationships between these thermodynamics laws through a series of mathematical deductions are given, which additionally result in the acquirement of the most important physical amounts of materials.

1.1 Thermodynamics of Materials Science, Scope and Special Features of the Book

Classical thermodynamics is a branch of physics originating in the nineteenth century as scientists were first discovering how to build and operate steam engines [1], which primarily led to the industrial revolution. A steam engine is a heat engine that performs mechanical work using steam as its working fluid. Historically, thermodynamics developed just out of needs to understand the nature of these heat engines and to increase the efficiency of transition between heat and work [2]. With a deeper understanding of the relationship between heat, work and temperature, the design of engines of specific power output and efficiency became possible. Although the relationship between science and technology in this period is complex, it is fair to say that without the introduction of scientific thermodynamic methods, the development of the industrial revolution would not have been so swift.

The demands of the industrial revolution had put the “standard model” of physics in a crisis around the question of “what is energy?”. Energy as the capacity to do work is essentially an abstract concept. It cannot be measured directly and thus has no definite value. Thermodynamics, dealing with energy and its transitions, is based on two laws of nature, namely the first and the second laws of thermodynamics [3]. Thermodynamics tells us that the energy differences can be measured by heat and work removed or added.
Heat and work are not stored as such anywhere, but are the two forms of energy transfer. Such results of thermodynamics meant that physics could be rewritten in terms of energy. Therefore, thermodynamics is one of the most basic sciences with applications in all fields of science and technology since its results are essential for physics, chemistry, materials science, chemical engineering, aerospace and mechanical engineering, cell biology, biomedical engineering, and economics [4].

In wide range of applications of thermodynamics, the scientific discipline that intersects the areas of materials science and thermodynamics is commonly known as thermodynamics of materials. Materials science involves investigating relationships of materials between manufacture, compositions and structures, properties, and performance [5]. The major determinants for materials structures and thus their properties are their constituent elements and the way in which they have been processed into their final forms as well as their activity between the manufactured parts and working surroundings. The development of thermodynamics both drove and was driven by atomic theory and even by quantum mechanics. The development of thermodynamics also motivated new directions in probability statistics. Atomic theory tells us that the electrons in the constituent elements occupy a set of stable energy levels and can transform between these states by absorbing or emitting photons that match the energy differences between the levels. Such electron structure of the individual atoms in turn determined various types of atomic interaction bondings that exist among constituent atoms or molecules. Without a doubt, materials store energy through the arrangement and motion of the constituent atoms, and so the way that a material changes its atomic structure during undergoing a change in thermodynamic state is governed by the laws of thermodynamics. Thermodynamics thus affects materials microstructures, defect concentration, atomic ordering, etc. Altogether, energy has to do with materials science. Thermodynamics of materials just deals with the relationships between energy and matters and describes how the properties of materials are affected by thermodynamic processes. In many cases, thermodynamics of materials is a crucial factor to good engineering design and performance forecast of manufactured components, parts, devices, tools, machines, etc. [6].

The last 50 years witnessed progressive miniaturization of the components employed in the construction of devices and machines [7]. One of the most striking significance of miniaturizing a solid to nanometer scale is the tunability in physical and chemical properties compared with the corresponding more bulky solids. Miniaturization itself has also achieved evident progress in the fields of microelectronics or super-large-scale integration circuits (SLIC) along with constant speed of scaling to maximize transistor density due to the requirements for electrical and functional performances. As predicted by Moore's law, new technology generations have been introduced with a 2-year or 18-month cycle, and packing density and device speed have increased exponentially at rapidly decreasing cost per function [8]. Today,
45 nm process technology is the world’s normal chip-manufacturing technology, where on-chip interconnect networks include eleven metal levels and connect more than $10^7 / \text{mm}^2$ transistors for 70 Mbit static random access memory (SRAM) chips [9]. Moreover, in one of the biggest advancements in fundamental transistor design, Intel used different transistor materials to build 731 million transistors inside the present generation of the company’s Intel Core i7 family in November, 2008 with 45 nm technique. Minimum feature sizes of the silicon technology are reduced to 32 nm in 2009. It is further envisioned that this size will be 22 nm in 2011 and 15 nm in 2013, while the ultimate feature sizes could be below 10 nm [8]. Nanomaterials have also been and will be widely utilized in medicine fields. For instance, nanoparticles have properties that are useful for the diagnosis and treatment of cancer, including their size-dependent properties, stability in solvent, ideal size for delivery within the body, and tunable surface chemistry for targeted delivery. Several different nanoparticle building blocks possessing varied functionalities can be assembled into one multifunctional composite nanoparticle, further expanding their potential use in cancer diagnostics and therapeutics [10].

With the large surface-to-volume ratio, the surface, interface, and quantum effects make such microscopic and mesoscopic systems differ substantially from isolated atoms of their constituent elements or the corresponding bulk counterparts in performance. The quantities, such as the phase transition temperature, the Young’s modulus, and the extensibility of a solid, are no longer constant but change with the materials size. Properties of nanomaterials determined by their shapes and sizes are indeed fascinated and form the basis of the emerging field of nanoscience and nanotechnology that have been recognized as the key area being of significance in science, technology, and economics in the 21st century. Thus, as the bridge between the atomic and macroscopic scales, the microscopic and mesoscopic systems have attracted tremendous interest in recent years because of their novel mechanical, thermal, acoustic, optical, electronic, dielectric, and magnetic properties from a basic scientific viewpoint, as well as from their great potential in upcoming technological applications such as SLIC and nano-electromechanic systems (NEMS). Accordingly, a huge experimental database has been generated for nanothermodynamics in past decades [10 – 13].

The physical and chemical properties of a macroscopic system can be well described using the classical thermodynamics in terms of the Gibbs free energy or the continuum medium mechanics. At the atomic scale, the quantum effect becomes dominant and the physical properties of a small object can be reliably optimized in computations by solving the Schrödinger equations for the behavior of electrons or the Newtonian motion of equations for the atoms with a sum of averaged interatomic potentials as key factors to the single body systems. However, for a small system at the nanometer regime, called mesoscopic or furthermore microscopic system, both the classical and quantum approaches encountered severe difficulties [10, 11].

Unfortunately, the unusual behavior of a nanostructure goes beyond the
expectation and description of the classical theories in terms of the continuum medium mechanics and the statistic thermodynamics. As the nanothermodynamics is an emerging field of study, fundamental progress is lagging far behind the experimental exploitations. Many questions and challenges are still open for discussion. Extending the validity of thermodynamics into nanometer size range thus becomes an urgent task. It is fascinating that the new variable of size and its combination with various thermodynamic parameters not only offer us opportunities to tune the physical properties of nanomaterials, but also allow us to gain information that may be beyond the scope of conventional approaches. Therefore, to complement the classical and the quantum theories, a set of analytical expressions from the perspective of nanothermodynamics for the size dependence of the intrinsic physical properties of a specimen is necessary where the size should be introduced as an independent variant [12]. This technique to extend the suitability range of the classic thermodynamics is usually called “top-down method”. It is noteworthy that since scientists and engineers in the long history have been familiar to the classic thermodynamic theory, for the most people, especially for materials scientists and engineers, using an extension of the classic thermodynamics theory is a much easy way compared with other theories to go into the nanoworld theoretically.

Based on the four thermodynamic laws, two essential and two additional, thermodynamics gives a number of exact relationships between many properties of materials. However, they are a theoretical construction, and new properties cannot be measured, but just be calculated. To get numerical answers, the theoretical framework has to be connected to the behavior of matters through properties that can be measured. However, before the advent of computers, only limited descriptions of matters were possible. Computer simulation as a new powerful technique could supply not only the details of atomic structures, but also the corresponding electronic states. Thus, computer simulation could support and make up the modeling results of nanothermodynamics. The use of computers starting around 1960 showed a gradual and even a dramatic change for thermodynamics, and is now practiced. It became increasingly possible to correlate data in proper models and then to use these models in combination with the rigorous thermodynamic relations with better answers. Almost all thermodynamic theories now rely on simulation techniques. This method has been named “bottom-up method” [14].

Some thermodynamic properties are easier to understand and explain based on the macroscale, while other phenomena are more easily illustrated at the microscale. Macro- and microscale investigations are just two views of the same thing. “Bottom-up method” together with “top-down method” guarantees development of nanothermodynamics or mesoscopic thermodynamics in recent years.

The book will start here in Chapter 1 with an introduction to the subject of macroscopic thermodynamics of materials and development of fundamental principle of four thermodynamics laws, which are essential for the
later chapters. Chapter 2 discusses the microscopic point of view: statistical mechanics, and how microscopic and macroscopic properties are connected. Chapter 3 shows the thermodynamic descriptions of heat capacity and entropy in solid, both are elementary parameters for many physical properties of matters. Alloying of elements and compounds leads to the presence of many interesting properties. In addition, some important chemical reactions take place not among pure elements or compounds, but among elements or compounds dissolved in one another as solution. A knowledge and understanding of phase diagrams are thus important to the engineers relating to the design and control of the heat treatment procedure. Furthermore, the development of a set of desirable mechanical characteristics for a material often results from a phase transition with the help of the heat treatment technique. Chapter 4 and Chapter 5 deal with thermodynamics of solution, phase diagrams, and phase transitions. Thermodynamic definitions of interface energy and interface stress are clarified to formulate surface thermodynamics [10, 11]. This theme becomes more and more important due to the appearance of nanotechnology. In Chapter 6, the interface thermodynamics is developed. In all later three chapters, the basic underlying principle of thermodynamics is applied to the behavior of all classes of materials, such as metals and alloys, ceramics, semiconductors and polymers. An important characteristic of this book is accentuation of a physical basis of thermodynamics. This is partly because of the development of physical theory, which makes it possible to analyze, illustrate and understand the physical nature of materials and materials properties. This book acts also as an authored advanced text, including authors’ research production in the new topics of nanothermodynamics or size effect of thermodynamic functions. Thus, authors intend to provide integrated approach to macro-(or classical), meso- and nano-, and microscopic (or statistical) thermodynamics.

1.2 Concepts of Thermodynamics [6, 15–17]

Thermodynamics is one of the basic sciences, which mathematically and quantitatively deals with heat and work and their transfer of materials in equilibrium, materials transitions, and their relationships with properties of materials. The thermodynamics consists of four essential laws that govern the study of energetic transitions and the relationships between thermodynamic properties [2, 3]. Two of these – the first and the second laws – dispose energy, directly or indirectly. Consequently they are of fundamental importance in materials studies of energy transitions and usage. The remaining two statements – the zeroth and the third laws – refer to thermodynamic properties and possess a second importance. The power of thermodynamics is that everything follows from these laws although it is hard for people to clarify how this is followed. By logical reasoning and skillful manipulation of these laws, it
is possible to correlate many properties of materials and to gain insight into many chemical and physical changes that materials undergo. In this chapter, we shall develop the principles of thermodynamics and show how they apply to a system of any nature.

There are a number of terms used in the study of thermodynamics and these concepts and terms are basilic in thermodynamic studies, hence their physical meanings must be clear and will be introduced in the following section.

As the word used in thermodynamics, a system is a part of the universe under consideration. A real or imaginary boundary separates the system from the rest of the universe, which is referred to as the environment. A useful classification of thermodynamic system is based on the nature of the boundary and the flows of matter, energy and entropy through it. There are three kinds of systems, depending on the kinds of interchanges taking place between a system and its environment. If condition is such that no energy and matter interchange with the environment occurs, the system is said to be isolated. If there are interchanges of energy and matter between a system and its environment, the system is named being open. A boundary allowing matter exchange is called permeable. The ocean would be an example of an open system. If there is only interchange of energy (heat and work) crossing the boundary, the system is called closed. A greenhouse is for instance such a system where exchanging energy with its environment is present while substances keep constant. Whether a system interchanges heat, work or the both is usually thought to be a property of its boundary, which may be adiabatic (not allowing heat exchange) or rigid boundary (not allowing exchange of work). In reality, a system can never be absolutely isolated from its environment, because there is always at least some slight coupling, even if only via minimal gravitational attraction.

The state of a thermodynamic system at any instant is its condition of existence at that instant, which is specified by values of a certain number of state variables or properties. Different properties that can be used to describe the state of a system comprise energy, entropy, chemical composition, temperature, pressure, volume, external field and substance size. The specification of the state of the system must include the values of these properties. A state of the system, which can be reproduced, means that the state is well defined.

A property of a system depends only on the state of the system, and not on how that state was attained. The uniqueness in the value of a property at a state introduces naming state function for a property. By contrast, the so-called path functions are quantities, which concern the path of a process by which a system changes between two states. Since a property is a state function, its differential must be an exact or perfect differential in a mathematical term. The line integral of the differential of a property is independent of the path or curve connecting the end states, and this integral vanishes in the special case of a complete cycle.
Thermodynamic properties of a system may be classified as intensive and extensive properties. The former is independent of the extent or mass of the system and can be specified at a specific point in the system, such as pressure, temperature, and specific volume. The latter is not additive because it does not scale with the size of the system and cannot be specified at a particular point of space. Its value for the entire system is equal to the sum of its values for all parts of the system. Volume, energy, and mass are instances of extensive properties. To change the latter to the former is generally done by normalizing the former by the size of the system, namely, by making the property be a density.

For our purpose, the energy of a system can be divided into three categories: internal, potential, and kinetic energy. To take them in a reverse order, kinetic energy refers to the energy possessed by the system due to its overall motion, either translational or rotational. The kinetic energy to which we refer is that of the entire system, other than that of the molecules in the system. For instance, if the system is a gas, the kinetic energy is the energy due to the macroscopic flow of the gas, not the motion of individual molecules. A familiar form of this energy is the translational energy of \((1/2)mv^2\) possessed by a body of mass \(m\) moving at a velocity \(v\).

The potential energy of a system is a sum of the gravitational, centrifugal, electrical, and magnetic potential energy. To illustrate this, the gravitational potential energy is taken as an example. A 1 kg mass, 10 m above the ground, clearly has a greater potential energy than the same mass on the ground. The potential energy can be converted into other forms of energy, such as the kinetic energy, if the mass is allowed to fall freely. The sizes of kinetic and potential energy lies in the environment in which the system exists. Particularly, the potential energy of a system depends on the choice of an arbitrarily chosen zero level. However, the difference in the potential energy, such as that between the mass at 10 m and that at the ground level, is the same and is independent of the datum plane.

The internal energy of a thermodynamic system, denoted as \(U\), is the sum of all microscopic forms of energy of a system. It is related to the molecular structure and degree of molecular activity and may be viewed as the sum of kinetic and potential energy of the molecules. \(U\) includes the energy in all chemical bonds, and the energy of the free, conduction electrons in metals. \(U\) of a system depends on the inherent qualities, or properties, of materials in the system, such as composition and physical form, as well as the environmental variables (temperature, pressure, external fields, system size, etc.). \(U\) has many forms, including mechanical, chemical, electrical, magnetic, surface, thermal, and size ones. For example, a compressed spring has higher internal energy (mechanical energy) than a spring without compression because the former can do some work on changing (expanding) to the uncompressed state.

On the question of thermal energy, it is intuitive that \(U\) of a system increases as its temperature \(T\) increases. The form of \(U\) of a material relating to its \(T\) is called thermal energy, not heat. Note that heat is the energy in
transfer between a system and the environment. Thermal energy is possessed by the system, and is a state function of a system and an extensive quantity. The SI unit of the energy is the joule.

The entire structure of the science of classical thermodynamics is built on the concept of equilibrium states. When a system is in equilibrium, unbalanced potential (or driving force), which tends to promote a change of state, is absent. The unbalanced potential may be mechanical, thermal, chemical or any combination of them. When temperature gradient is absent in a system, the system should be in a state of thermal equilibrium, which is the subject of the zeroth law of thermodynamics. If there are variations in pressure or elastic stress within the system, parts of the system may move, either expand or contract. Eventually these motions (expansion or contraction) will cease. When this has happened, the system is in mechanical equilibrium. If a system has no tendency to undergo either a chemical reaction or a process such as diffusion or solution, the system is regarded as in a state of chemical equilibrium. If all these equilibrium is satisfied, the system is in a state of thermodynamic equilibrium.

In the most part of this book, we shall consider systems that are in thermodynamic equilibrium, or those in which the departure from thermodynamic equilibrium is negligibly small. The local state of a system at thermodynamic equilibrium is determined by the values of its intensive parameters, such as pressure $P$, $T$, and system size (radius) $r$, etc. Specifically, thermodynamic equilibrium is characterized by a minimum of a thermodynamic potential. Usually the potential is the Helmholtz free energy, i.e. system is in a state at constant $T$ and volume $V$. Alternatively, the Gibbs free energy can be taken as the potential, where the system is at constants $P$ and $T$.

When any property of a system is changed, the state of the system varies, and the system undergoes a process. A thermodynamic process may be defined as the energetic evolution of a thermodynamic system from an initial to a final state. Paths through the space of thermodynamic properties are often specified by holding certain thermodynamic variables as constants. It is useful to group these processes into pairs, in which each variable holding constant is one member of a conjugate pair. For instance, $P$-V conjugate pair is concerned with the transfer of mechanical or dynamic energy as the result of work.

An isobaric process is a thermodynamic process in which $P$ stays constant: $\Delta P = 0$ where $\Delta$ shows the difference. The heat transferred to the system does work but also changes $U$ of the system, such as a movable piston in a cylinder. In this instance, $P$ inside the cylinder is always at atmospheric pressure, although it is isolated from the atmosphere. In other words, the system is dynamically connected, by a movable boundary, to a constant-pressure reservoir.

An isochoric process is one where $V$ is held constant, meaning that the mechanical work done by the system $W$ is zero. It follows that for a simple system of two dimensions, any heat energy transferred to the system
externally will be absorbed as $U$. An isochoric process is also known as an isometric or isovolumetric process. An example would be to place a closed tin can containing only air into a fire. To the first approximation, the can will not expand, and the only change is that the gas gains $U$, as evidenced by its increase in $T$ and $P$. We may say that the system is dynamically insulated from the environment by a rigid boundary.

The temperature-entropy ($T$-$S$) conjugate pair is concerned with the transfer of thermal energy as the result of heating.

An isothermal process is a thermodynamic process where $\Delta T = 0$. This typically occurs when a system is in contact with an outside thermal reservoir (heat bath), and processes occur slowly enough to allow the system to continually adjust to $T$ of the reservoir through heat exchange. Having a system immersed in a large constant-temperature bath is such a case. Any work energy performed by the system will be lost to the bath, but its $T$ will remain constant. In other words, the system is thermally connected by a thermally conductive boundary to a constant-temperature reservoir.

An adiabatic process is a process where there is no heat transferred into or out of the system by heating or cooling. For a reversible process, this is identical to an isentropic process. Namely, the system is thermally insulated from its environment and its boundary is a thermal insulator. If a system has entropy which has not yet reached its maximum equilibrium value, $S$ will increase even though the system is thermally insulated.

During a thermodynamic process, some unbalanced potential exists either within the system or between it and the environment, which promotes the change of state. If the unbalanced potential is infinitesimal so that the system is infinitesimally close to a state of equilibrium at all times, such a process is called quasistatic. A quasistatic process may be considered practically as a series of equilibrium states and its path can graphically be represented as a continuous line on a state diagram. By contrast, any process taking place due to finite unbalanced potentials is non-quasistatic.

A system has undergone a reversible process if at the conclusion of the process, the initial states of the system and the environment can be restored without leaving any net change at all elsewhere. Otherwise, the process is irreversible. A reversible process must be quasistatic, so that the process can be made to traverse in the reverse order the series of equilibrium states passed through during the original process, without change in magnitude of any energy transfer but only a change in direction.

The most natural processes known to be reversible are an idealization. Although real processes are always irreversible, some are almost reversible. If a real process occurs very slowly, the system is thus virtually always in equilibrium, the process can be considered reversible.
1.3 Temperature and Zeroth Law of Thermodynamics

We often associate the concept of $T$ with how hot or cold a system feels when we touch it. Thus, our senses provide us with qualitative indications of $T$. However, our senses are unreliable and often misleading. We thus need a reliable and reproducible method, which makes quantitative measurements establish the relative “hotness” or “coldness” of systems that is solely related to $T$ of the system.

After the three laws of thermodynamics were explained practically and theoretically, the scientists tried to make thermodynamics systematically logical. It was realized that a basic statement about $T$ was important and even more fundamental. This statement is given the unusual name of the zeroth law of thermodynamics: When two systems are each in thermal equilibrium with a third system, the first two systems are in thermal equilibrium with each other.

The above statement implies that all systems have a physical property that determines whether or not they will be in thermal equilibrium when they are placed in contact with other systems. This property is called temperature. Two systems in thermal equilibrium with each other are at the same $T$. Thus, thermometers can be called the “third system” and used to define a temperature scale. The thermometer as a device is used to measure $T$ of a system, with which the thermometer is in thermal equilibrium. All thermometers make use of some physical properties exhibiting a change with $T$ that can be calibrated in order to make $T$ measurable. Some of the physical properties used are (1) $V$ of a liquid, (2) the length of a solid, (3) $P$ of a gas held at constant $V$, (4) $V$ of a gas held at constant $P$, (5) the electric resistance of a conductor, and (6) the color of a very hot object. For instance, $V_L$, the volume of a liquid, is taken as such physical property in the familiar liquid-in-glass mercury or alcohol thermometers. The thermometers used most widely in precise experimental work are however the resistance thermometer and the thermocouple.

Another important type of thermometer, although it is not suitable for routine laboratory measurements, is the constant volume gas thermometer. The behavior observed in this device is $P$ variation with $T$ of a fixed $V$ of gas. When the constant volume gas thermometer was developed, it was calibrated using the ice and steam points of water. $P$ and $T$ values are then plotted on a graph, as shown in Fig. 1.1.

The line connecting the two points serves as a calibration curve for measuring unknown $T$. To measure $T$ of a substance, we place the gas thermometer in thermal contact with the substance and measure $P$ of the gas. Then, $T$ of the substance from the calibration curve can be found.

If the curves in Fig. 1.1 are extended back toward negative $T$, we find a starting result. In any case, regardless of the type of gas or the value of the low starting $P$, $P$ extrapolates to zero when the Celsius temperature $T_C$ is $-273.15 \, ^{\circ}C$. This suggests that this particular $T$ is universal in its importance,
which does not depend on the substance used in the thermometer. In addition, since the lowest $P = 0$, which would be a perfect vacuum, this $T$ must represent a lower bound for physical processes. Thus, we define this $T$ as the starting point of the absolute or the thermodynamic temperature, which is utilized as the basis for the Kelvin temperature scale $T = t_C - 273.15 ^\circ C = 0 \text{ K}$. The size of one “degree” in the Kelvin scale (called a Kelvin or one K) is chosen to be identical to the size of a degree in the Celsius scale. Thus, the relationship that enables us to convert between $t_C$ and $T$ is

$$t_C = T - 273.15.$$ 

Early gas thermometers made use of ice and steam points according to the procedure just described. However, these points are experimentally difficult to duplicate because they are pressure-sensitive. Consequently, a procedure based on two new points was adopted in 1954 by the International Committee on Weights and Measures. They are 0 K and the triple point of water where water, water vapor, and ice coexist in equilibrium with a unique $T$ and $P$. This convenient and reproducible reference $T$ for the Kelvin scale is $t_C = 0.01 \ ^\circ \text{C}$ or $T = 273.16 \text{ K}$ and $P = 4.58 \text{ mmHg}^{\dagger}$. Thus, the SI unit of $T$ is defined as $1/273.16$ of this triple point.

1.4 First Law of Thermodynamics [6, 17, 18]

The first law of thermodynamics is essentially the law of conservation of energy applied to thermodynamic systems. Through his famous experiments in 1843 Joule was led to the postulate that heat and work were of equivalent quantities, which is generally known as the first law of thermodynamics. This

\[ 1 \text{ mmHg} = 1.33322 \times 10^2 \text{ Pa}. \]
law is most simply stated as “energy cannot be created or destroyed” or “the energy of the universe is a constant”. More precise statement is for instances: “a given amount of energy in a particular form can be converted to energy of a different form and then transformed back into the same amount of the original form. The total energy during the conversion and reverse process is constant”. Remember that the first law states that energy is conserved always. It is a universally valid law for all kinds of processes and provides a connection between microscopic and macroscopic worlds.

In thermodynamics of materials, we are most interested in the transitions of energy and how it governs the interaction of energy with materials. We know that as a material changes its structure or as individual atoms of the material increase their motion, the energy of the material changes. However, this energy change must be balanced by an equal and opposite variation in energy of the environment. Thus, although we haven’t developed much detail of how energy and materials interact, we do know that the total energy is a constant throughout the process regardless of the details of their interaction.

According to the first law of thermodynamics, it is useful to separate changes to $U$ of a thermodynamic system into two sorts of energy transfers: heat $Q$ and work $W$. Both indicate path dependent quantities. They only have meaning when describing a property of the process, not the state of the system. We cannot tell what the heat of a system is. We can however tell what heat is associated with a well defined process. Neither heat nor work is the energy contained in a system and neither is a system property. The differential of a path function is inexact and is denoted by the symbol $\delta$ to distinguish from the symbol $d$ for exact differentials.

$Q$ is a form of energy exchange between a system and its environment. Heat flows from regions of high $T$ to that of low $T$. So like $P$, $T$ is a potential for transferring energy, specifically the potential to transfer energy as $Q$. $Q$ is a mechanism by which energy is transferred between a system and its environment due to the existence of $\Delta T$ between them. The algebraic sign of $Q$ is positive when heat flows from the environment into the system. The increase in $T$ of the system is caused by an increase in the thermal energy of the system. In a thermodynamic sense, heat is never regarded as being stored within a system. When energy in the form of heat is added to a system, it is stored not as heat, but as kinetic and potential energy of the atoms or molecules making up the system.

From an atomic point of view, heat is the transfer of energy that occurs through the chaotic motion of matters at a molecular scale. The atoms in a hot region of a material vibrate chaotically more than that in a cooler region of the material. As atoms vibrate, they impart a force to their neighbors and cause them to move. The hotter the atoms, the more vigorous the motions and the larger the forces they impose on their neighboring atoms. This random motion passing from one point to another in the material results in energy transfer and eventually brings out a uniform amount of chaotic motion once the random motion of energetic atoms has flowed so that no
temperature gradients persist. This transfer of kinetic energy to neighboring atoms accomplished through flow of random atomic motion is called heat transfer. Random, chaotic motion is thus disordered and is classified as thermal motion, whereas work causes ordered, organized motion of the atoms in a system in a uniform manner.

The work-energy principle, in mechanics, is a consequence of Newton’s law of motion. It states that the work of the resultant force on a particle is equal to the change in kinetic energy of the particle. If a force is conservative, the work of this force can be set to equal the change in potential energy of the particle, and the work of all forces exclusive of this force is equal to the sum of the changes in kinetic and potential energy of the particle.

Work can also be done in a process where there is no change in either the kinetic or potential energy of a system. Work is thus done when a gas is compressed or expanded, or when an electrolytic cell is charged or discharged, or when a paramagnetic rod is magnetized or demagnetized, even though the gas, or the cell, or the rod, remains at rest at the same elevation. Thermodynamics is largely (but not exclusively) concerned with processes of this sort where the work is defined as all other forms of energy transferred between the system and its environment by reasons other than a temperature gradient.

In mechanics, the work is defined as the product of a force and the displacement when both are measured in the same direction. When a thermodynamic system undergoes a process, the work in the process can always be traced back ultimately to the work of some force. Mechanical work $W$ can be made on the system, say, by compressing the system (volume changes). Electrical work being done on the system is the moving charges in the system by the application of an external electric field. Thus, it is convenient to express the work in terms of the thermodynamic properties of the system and we first seek to derive the expression for work in relation to volume changes.

Consider the compression of a gas in a cylinder of an automobile engine. If the gas is taken as the system, work done on the system is by the face of the piston, whose magnitude is the force $f_o$, multiplied by the distance $\Delta l$ through which the piston moved (Fig. 1.2).

![Fig. 1.2 Mechanical work.](image)

If the cross-sectional area of the piston is taken as $A$, the gas pressure
against the piston is $P$, this work term $W$ can be converted into

$$W = -f_0\Delta l = -PA\Delta l = -P\Delta V, \text{ or } \delta W = -PdV. \quad (1.1)$$

Note that $W$ is done on a system when there is a pressure gradient where $P$ is the potential to do the mechanical work. $W$ is expressed in a unit J ($=\text{N}\cdot\text{m}$) when $P$ is expressed in a unit N·m$^{-2}$, or pascal (Pa), and the volume change $\Delta V$ is expressed in unit m$^3$.

The direction of force and the distance moved establishes the algebraic sign of $W$, which is defined as being positive when work is done on a system by the environment. $W < 0$ when the system does work on the environment. Thus negative sign in Eq. (1.1) insures that when system is compressed, $W$ is positive since $\Delta l$ will be negative. The sign convention is the same for both $Q$ and $W$, that is, these terms are considered to be positive when they add energy to the system.

There are a number of other work modes that occur frequently in thermodynamic analyses. Consider next a specialized mechanical system with work modes other than $-PdV$. The work done in stretching an elastic thin solid rod or wire consists of $A$ and $l$ where $V_0 = Al$ is the volume of the rod at the unstrained state. If the stretching force $f_0$ acts through an elongation $dl$, the work input is $\delta W = f_0dl$. It is appropriate in the study of elastic solids to express work in terms of the stress $\delta$ and the strain $\varsigma$ where $\delta = f_0/A$ and $d\varsigma = dl/l$. Upon substituting these equations into the expression for work, we get the work of elastic stretching $\delta W = Al\delta d\varsigma$, or,

$$\delta W = V_0\delta d\varsigma. \quad (1.2)$$

One important application of thermodynamics is the study of the behavior of paramagnetic substances at extremely low $T$. This issue will be considered more fully in Secs. 2.5.2 and 3.1.2, and for the present we discuss only the expression for the work in a process where the magnetic state of the material in a magnetic field is changed. To start with this theme, several essential concepts of the magnetism are simply clarified. Just as an electron current in a small loop produces a magnetic field, an electron revolving in its orbit around the nucleus and rotating around its own axis has associated a magnetic dipole with its motion. In the absence of an external magnetic field, all such dipoles cancel each other. In the presence of an external field, however, the frequencies and senses of orbiting and spinning of the electrons will be changed in such a manner as to oppose the external field. This is the diamagnetic nature of all materials. In some materials, however, there are permanent magnetic dipoles owing to unbalanced electron orbits or spins. These atoms behave like elementary dipoles, which tend to align with an external field and to strengthen it. When this effect in a material is greater than the diamagnetic tendency common to all atoms, this material is termed paramagnetic. Note that paramagnetism is $T$-dependent. When $T$ is sufficiently lower, the atomic elementary dipoles are magnetically aligned within microscopic domains, which can be readily aligned by a relatively small external
field $H_{\text{mag}}$ to form a large induction. This is referred to as ferromagnetic. A ferromagnetic material becomes paramagnetic above a $T$ known as the Curie temperature $T_C$. $T_C$ of Fe, Co, and Ni are far above room temperature; they are thus usually referred to as ferromagnetic. On the other side, some metallic salts with $T_C < 1 \text{ K}$ are usually considered as paramagnetic. A paramagnetic material is not a magnet if there is no $H_{\text{mag}}$ applied to it. Under an external field, it becomes slightly magnetized in contradistinction to a ferromagnetic material, which shows very strong magnetic effects.

In ferromagnetic materials, each atom has a comparatively large dipole moment caused primarily by uncompensated electron spins. Interatomic forces produce parallel alignments of the spins over regions containing large numbers of atoms. These regions or domains have a variety of shapes and sizes (with dimensions ranging from a micron to several centimeters), depending on materials and magnetic history. The domain moments are generally randomly oriented, the material as a whole has therefore no magnetic moment. Under $H_{\text{mag}}$, however, those domains with moments in the direction of the applied $H_{\text{mag}}$ increase their sizes at the expense of their neighbors, and the internal field becomes much larger than $H_{\text{mag}}$ alone. When $H_{\text{mag}}$ is removed, a random domain alignment in the material does not usually occur, and a residual dipole field remains. This effect is called hysteresis. The magnetic effects on a ferromagnetic material are not reversible because the reverse process of demagnetization forms a hysteresis loop with the forward process of magnetization. Thus, the state of a ferromagnetic system relies on not only its present condition, but also its past history. A ferromagnetic system is thus not amenable to thermodynamic analyses. On the other hand, the magnetization process is reversible and the state of the system can be described by a few thermodynamic variables for a paramagnetic system (such as a paramagnetic salt) or a diamagnetic system (such as a superconducting material). Most experiments on magnetic materials are performed at constant $P$ and involve insignificant volume changes. Hence, variations of $P$ and $V$ can be ignored.

When the system consists of a long slender rod in an $H_{\text{mag}}$ parallel to its length $l$ with cross-sectional area $A$, demagnetizing effects can be neglected. Suppose it is to be wound uniformly with a magnetizing winding of negligible resistance, having $N$ turns and carrying a current $I$. $H_{\text{mag}} = NI/l$ set up by $I$ in the winding, which in turn produces a magnetic induction $B$, being the flux density in the rod. $\Phi = BA$ is the total flux. If $I$ is changed by $dI$, in time interval $dt$, the flux is varied by $d\Phi$, there is an induced back electromotive force (emf) $\varepsilon_{\text{emf}}$ according to the relation $\varepsilon_{\text{emf}} = -Nd\Phi/dt = -NA dB/dt$ in terms of Faraday’s law of electromagnetic induction. A quantity of electricity $dq$ is transferred in the circuit during $dt$, the work done by the system is thus $\delta W = -\varepsilon_{\text{emf}} dq = NA(dq/dt) dB = NA dB$. Combining the preceding equation of $H_{\text{mag}} = NI/l$, it gives $\delta W = VH_{\text{mag}} dB$ with $V = Al$.

If $\mu_v$ is the magnetization in the rod, or the magnetic moment per unit volume, $B$ in the core becomes $B = \mu_0(H_{\text{mag}} + \mu_v)$, where $\mu_0 = 4\pi \times 10^{-7}$
N·A$^{-2}$ is permeability of free space. The magnetic moment is present since the originally random distribution of orbital and spin motions of electron under an $H_{\text{mag}}$ reorientates. When this expression for $B$ is inserted in the $\delta W$ equation, $\delta W = \mu_0 V H_{\text{mag}} dH_{\text{mag}} + \mu_0 V H_{\text{mag}} d\mu_v$. When there is no material within the winding, $\mu_v = 0$, and the right-hand side of the equation is reduced to the first term only, or $\mu_0 V H_{\text{mag}} dH_{\text{mag}}$ is the work required to increase the magnetic field of the empty space of $V$ by an amount $dH_{\text{mag}}$. The second term on the right is therefore the work associated with the change in magnetization of the rod. Because we are interested in the thermodynamics of the material, the work of magnetization, exclusive of the vacuum work, is simply $\delta W = \mu_0 V H_{\text{mag}} dp_m$, which can be written in terms of the total magnetic moment $M = \mu_0 V \mu_v$, namely,

$$\delta W = H_{\text{mag}} dM. \quad (1.3)$$

Equation (1.3) indicates that work input is required to increase the magnetization of a substance.

Next, we take the work of polarization into account. In contrast with an electric conductor having a sufficiently large number of free electrons, a dielectric or electric insulator has none or only a relatively small number of free electrons. The major effect of an electric field on a dielectric is the polarization of the electric dipoles. Work is done by $H_{\text{mag}}$ on the dielectric material during the polarization process.

For the purpose of deriving the equation of work in polarizing a dielectric, let us consider a parallel-plate capacitor or condenser. The two plates, each of area $A$ with a distance of separation $l$, are charged with equal and opposite charges $\pm q$. According to electrostatics, when the space between the plates is a vacuum, the electric field intensity $E_e$ created by the charges is given by $E_e = q/(A\varepsilon_0)$, where $\varepsilon_0 = 8.85 \times 10^{-12} \text{ C}^2\text{N}^{-1}\text{m}^{-2}$ is the permittivity of a free space. $u = E_e l = ql/(A\varepsilon_0)$ where $u$ is the potential difference between the plates.

Let a dielectric material be inserted between the plates. In the absence of $E_e$, in spite of the atomic irregularities, we can imagine the dielectric to be composed of generally uniform distributions of positive and negative charges. Under the influence of an $E_e$, a rearrangement of the charges in the dielectric takes place and it thus becomes polarized. The positive charges are displaced slightly in the direction of the field, while the negative charges are done in the opposite direction. Thus, because of the presence of the dielectric between the capacitor plates, the effective charge on each plate is reduced by a relative permittivity $\varepsilon_r$. The actual permittivity of dielectric is then calculated by multiplying the relative permittivity by $\varepsilon_0$, $\varepsilon_a = \varepsilon_r \varepsilon_0 = (1 + \chi)\varepsilon_0$, where $\chi$ is the electric susceptibility of the dielectric. Hence, the electric field and the potential difference between the plates are described by the equation $E_a = q/(A\varepsilon_a)$ and $u = ql/(A\varepsilon_a)$.

The electric polarization $P_d$ of a dielectric is defined as the electric dipole moment per unit volume and is related to $E_a$ by $P_d = \varepsilon_0 \chi E_a$, while $P_d$ and
1.4 First Law of Thermodynamics

$E_e$ in turn are related to the electric displacement $l_{ed}$, which can be separated into a vacuum contribution and the one arising from the dielectric by $l_{ed} = \varepsilon_a E_a = \varepsilon_0 E_e + P_d = q/A$. The reversible work done in charging a capacitor is $\delta W = u dq$, which may be transformed to $\delta W = (E_e l_e) d(l_{ed}) = (A l_e E_e d l_{ed} = V E_e d l_{ed})$. Combining the preceding equation with $l_{ed} = \varepsilon_0 E_e + P_d$, it gives

$$\delta W = V\varepsilon_0 E_e dE_e + V E_e dP_d.$$  

(1.4)

When there is no material between the capacitor plates, $P_d = 0$, $\delta W = V\varepsilon_0 E_e dE_e$ and $V\varepsilon_0 E_e dE_e = d(V\varepsilon_0 E_e^2/2)$ is the work required to increase the electric field of the free space between the capacitor plates by an amount $dE_e$. This quantity is additive to $U$ when the first law is used. Therefore, with $P_d' = VP_d$, the reversible work in the polarization of a dielectric is

$$\delta W = V E_e dP_d = E_e dP_d'.$$  

(1.4)

As a final example of a process, in which work other than mechanical one ($-P_d V$) is done, take into account the work of surface when the area of a surface $A$ for a film with thickness $2r$ is changed,

$$\delta W = \gamma_{sv} dA = 2\gamma_{sv} dV/r$$  

(1.5)

where $\gamma_{sv}$ is surface energy or solid-vapor interface energy. Note that $r$ could be extended as a radius for a particle or a wire. Equation (1.5) is especially important when material size is considered as a variant, which will come into contact with nanothermodynamics and will be discussed in detail in Chapter 6.

Since work can be done by many different kinds of forces, to find the total work, we add together the mechanical, magnetic, electrical, and surface work, etc. That is $\delta W_{total} = \delta W + \delta W' + \delta W'' + \cdots = -P_d V + H_{mag} dM + E_d P_d' + \gamma A + \cdots$. Let us define $\delta W^*$ as “useful” work exclusive of the $P_d V$ term, $\delta W_{total} = \delta W + \delta W^*$. Because we often focus on simple systems where only mechanical work is done on or by the system, $\delta W_{total} = \delta W = -P_d V$.

If we have a closed system and it is carried out through a cycle, the first law is expressed by

$$\oint \delta Q + \oint \delta W = 0, \quad \text{or} \quad \oint (\delta Q + \delta W) = 0.$$  

(1.6)

Since the cyclic integral of the quantity $(\delta Q + \delta W)$ is always zero, it is a differential of a property of the system and is a state function or a property of the system. This property is called the stored energy, which represents all energy of a system at a given state, such as the kinetic energy, potential energy and all other energy of the system. We call the energy the internal energy $U$. In the absence of motion and gravity effects, the first law for a closed system may be written in integrated form as

$$\Delta U = Q + W,$$  

(1.7)
or in a differential form
\[ dU = \delta Q + \delta W. \]  
(1.8)
The value of \( Q \) as a transfer quantity and a process variable depends on the process that the system undergoes during heat transfer. \( Q \) values of several simple processes are discussed here. From the first law and taking into account only mechanical work, we have
\[ \delta Q = dU + PdV. \]  
(1.9)
If \( dV = 0 \), there is no work done between the system and the environment, \( \delta W = 0 \). Hence, the heat flow into the system is just equal to the change in internal energy,
\[ \delta Q_V = dU, \quad \text{or} \quad Q_V = \Delta U. \]  
(1.10)
For an isometric process, the infinitesimal expression for heat forms an exact differential, but for processes involving work, it forms an inexact differential.

Although Eq. (1.10) is simple and convenient, many processes occur under a constant \( P \), rather than with a constant \( V \). This is because in many laboratory experiments a considered system is exposed to atmospheric pressure, rather than kept in vessel with a constant \( V \). If the process is isobaric (\( dP = 0 \)), from the first law and considering only mechanical work, then the heat associated with this process is \( \delta Q_P = dU + (PdV)_P = dU + d(PV) = d(U + PV) \). The term \( U + PV \) is defined as enthalpy \( H \),
\[ H \equiv U + PV. \]  
(1.11)
\( H \) in Eq. (1.11) has the unit of energy. \( H \) is a state function since \( U, P, \) and \( V \) all are. Finally,
\[ \delta Q_P = dH, \quad \text{or} \quad Q_P = \Delta H. \]  
(1.12)
For a system under a constant \( P \), \( \Delta H \) is the heat received by the system plus the useful work that has been done.

Although \( H \) is commonly used in engineering and science, it is impossible to directly measure it, while \( \Delta H \) is measured instead. For exothermic and endothermic reaction at a constant \( P \), \( \Delta H \) equals the energy released (negative) and absorbed (positive) in the reaction, respectively.

If \( \Delta V \) is little and \( P \) is not too big (these are the conditions of small \( PdV \)),
\[ dH = dU + PdV \approx dU. \]  
(1.13)
This is exactly the case we find for processes involving condensed phases under a low to moderate \( P \) where \( \Delta U \approx \Delta H \), which is often used in some theoretical calculations and computer simulations due to the simplicity.

When heat is transferred to a system, a change of \( U \) occurs, which can affect the kinetic energy or potential energy of the molecules, or both. We can define two types of heat: sensible and latent. Sensible heat \( Q \) causes a temperature change but the system does not change its phase. Latent heat
causes phase change with a constant $T$; for example, latent heat of boiling, latent heat of melting, etc.

$Q$ transferred to or from a system causes its $T$ changing from an initial value $T_{in}$ to a final value $T_{fi}$, which is calculated as follows: $Q = C \Delta T = C(T_{fi} - T_{in})$ where the proportionality constant $C$ is called the heat capacity. $C$ is the amount of heat energy required to increase the unit temperature of a substance in a unit of J-K$^{-1}$. $C$ is an extensive property because its value is proportional to the material amount in the system; for instance, a bathtub of water has a greater heat capacity than a cup of water. The heat capacity of a unit quantity of a substance is called specific heat capacity or specific heat, which becomes an intensive property and can be measured.

When the unit quantity is the mole, the term molar heat capacity $C_m$ in J-mol$^{-1}$-K$^{-1}$ may be used to describe the measure more explicitly. The equation relating heat energy to $C_m$ is

$$Q = nC_m \Delta T \quad (1.14)$$

where $n$ is the number of moles.

$C$ is mathematically defined as the ratio of a small amount of heat $\delta Q$ added to the system, to the corresponding small increase in its temperature $dT$,

$$C = \left( \frac{\delta Q}{dT} \right)_{\text{cond.}}. \quad (1.15)$$

For a real system, the path through energy changes must be explicitly defined, since $C_m$ value relies on which path from one $T$ to another is chosen. $C_m$ of substances are typically measured under constant $P$ ($C_{P,m}$). However, fluids (gases and liquids) are typically also done at constant $V$ ($C_{V,m}$). $C_{V,m}$ is determined by

$$C_{V,m} = \left( \frac{\delta Q_m}{dT} \right)_V = \left( \frac{\partial U_m}{\partial T} \right)_V. \quad (1.16)$$

Note that we have implicitly assumed that no other forms of work, such as electrical or magnetic, are involved. Accordingly,

$$dU = nC_{V,m}dT. \quad (1.17)$$

Measuring $C_{V,m}$ can be prohibitively difficult for liquid and solids. That is, $dT$ typically requires large $P$ to maintain a liquid or solid at constant $V$. This implies that the containing vessel must be nearly rigid or at least very strong. Instead it is easier to measure $C_{P,m}$ (allowing the material to expand or contract as it wishes). The thermal energy added to the material is accounted for by the increase in $U$ plus $W$ done by the material as it expands against the constant $P$ imposed on it. As a result,

$$C_{P,m} = \left( \frac{\delta Q_m}{dT} \right)_P = \left( \frac{\partial H_m}{\partial T} \right)_P. \quad (1.18)$$
1.5 Entropy and Second Law of Thermodynamics [6, 17, 18]

It is well known that physical processes in nature proceed toward equilibrium spontaneously. Liquids flow from a region of high elevation to that of low elevation; gases expand from a region of high $P$ to that of low $P$; heat flows from a region of high $T$ to that of low one, and material diffuses from a region of high concentration to that of low one. A spontaneous process can proceed only in a particular direction. Everyone realizes that these reversed processes do not happen. But why? The total energy in each case would remain constant in the reversed process as it did in origin, and there would be no violation of the principle of conservation of energy. There must be another natural principle, in addition to the first law, not derivable from it, which determines the direction, in which a natural process will take place. This principle is contained in the second law of thermodynamics, which epitomizes our experience with respect to the unidirectional nature of thermodynamic processes.

The invention and improvement of the steam engine and internal combustion engine, the devices that convert $Q$ into $W$, played an important role in the development of the second law. These devices also made industrial development possible, and greatly changed the nature of our everyday life. The first law accounts for the energy involved in such a conversion but places no limits on the amounts that can be converted. The second law is concerned with limits on the conversion of “heat” into “work” by heat engines. As one of the fundamental laws of nature, the second law cannot be derived from any other laws and may be stated in many different forms, but when its statement is accepted as a postulate, all other statements of it can then be proved. One of which, known as the Kelvin-Planck statement, is as follows: it is impossible to construct a heat engine that, operating in a cycle, produces no other effect than the absorption of energy from a reservoir and the performance of an equal amount of work. Its essence is that it is theoretically impossible to construct a heat engine that works with 100% efficiency.

Can we find some features all of the above dissimilar impossible processes have in common? What are the conditions under which no process at all can occur, and in which a system is in equilibrium? Is there any thermodynamic quantity that can help us to predict whether a process will occur spontaneously? These questions could be answered if some properties of a system, namely, some state functions of a system, have different values at the beginning and at the end of a possible process. A function having the desired property was devised by Clausius and is called entropy of the system $S$. The concept of $S$ is developed using the properties of the Carnot cycle and then calculating entropy changes $\Delta S$ during reversible and irreversible processes.

The principles governing heat engines were investigated in 1824 by a French engineer Sadi Carnot. Through considering an idealized heat engine,
now called a Carnot engine, Carnot found that a heat engine operating in an ideal, reversible cycle—called a Carnot cycle—is the most efficient engine possible. Such an engine establishes an upper limit on the efficiencies of all real engines. That means not all the heat removed from a high $T$ reservoir is converted into work. In fact, the amount that can be converted is governed by the temperatures of the two reservoirs.

The Carnot cycle consists of two reversible isothermal and two reversible adiabatic processes. From thermodynamic calculation, it was concluded that for any two temperatures $T_2$ and $T_1$, the ratio of the magnitudes of $Q_2$ and $Q_1$ and that of the magnitudes of $T_2$ and $T_1$ in a Carnot cycle have the same value for all systems, no matter whatever their nature is, where $Q_2$ is a heat flow into the system and $Q_1$ is a heat flow out of the system, namely,

$$ \frac{T_2}{T_1} = -\frac{Q_2}{Q_1}, \quad \text{or} \quad \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0. \quad (1.19) $$

A system undergoing a reversible cycle is presented by the continuous curve shown in Fig. 1.3. It is possible to subdivide this cycle into a number of small Carnot cycles as indicated. The isotherms and part of the adiabats of the small Carnot cycles form a zigzag curve which follows closely the path of the original cycle. The remaining parts of the adiabats of the small Carnot cycles cancel out because each section is traversed once in a forward direction and once in a reverse direction. As the number of Carnot cycles is increased, the zigzag curve can be made to approach the original cycle to any desired degree.

**Fig. 1.3** A reversible cycle subdivided into infinitesimal Carnot cycles.

Let $\delta Q_1, \delta Q'_1, \delta Q''_1, \ldots, \delta Q_2, \delta Q'_2, \delta Q''_2, \ldots$ denote the respective algebraic amounts of heat exchanged, which are positive when absorbed and negative when given off by the system. Then for the small Carnot cycles as we may
write \( \frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0 \), and \( \frac{\delta Q'_1}{T_1} + \frac{\delta Q'_2}{T_2} = 0 \), \( \ldots \), etc. Adding the preceding equations gives \( \frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} + \frac{\delta Q'_1}{T_1} + \frac{\delta Q'_2}{T_2} + \cdots = \sum \frac{\delta Q}{T} = 0 \). In the limit, upon replacement of the summation of finite terms by a cyclic integral, we obtain
\[
\oint \frac{\delta Q_{\text{rev}}}{T} = 0 \tag{1.20}
\]
where the subscript “rev” serves as a reminder that the result above is applied to reversible cycles only. The foregoing equation states that the integral of \( \delta Q/T \) when carried out over a reversible cycles is equal to zero. It follows that the differential \( \delta Q_{\text{rev}}/T \) is a perfect differential and the integral \( \oint \delta Q_{\text{rev}}/T \) is a property of the system. This property is called entropy \( S \), and
\[
dS = \frac{\delta Q_{\text{rev}}}{T}, \quad \text{or} \quad \delta Q_{\text{rev}} = TdS. \tag{1.21}
\]
Equation (1.21) is the defining expression for \( S \). Integrating along a reversible path between two equilibrium states 1 and 2 gives
\[
\Delta S_{12} = S_2 - S_1 = \int_{1}^{2} \frac{\delta Q_{\text{rev}}}{T}. \tag{1.22}
\]
It cannot be overemphasized that \( S \) is a state function; it depends only on the state that the system is in, and not on how that state is reached. If a system goes from state 1 to 2, its entropy changes from \( S_1 \) to \( S_2 \). However, it is only when the system travels along a reversible path between the two end states that Eq. (1.22) is valid. If the path is irreversible, \( \int_{1}^{2} (\delta Q_{\text{irr}}/T) \) differs from \( \Delta S_{12} \). The relation that does exist between the change in entropy and the integral \( \int_{1}^{2} (\delta Q/T) \) along any arbitrary path can be obtained as follows:
\[
dS \geq \frac{\delta Q_{\text{rev}}}{T}, \quad \text{or} \quad \Delta S_{12} = S_2 - S_1 \geq \int_{1}^{2} \frac{\delta Q}{T} \tag{1.23}
\]
where the equality holds for a reversible process and so does the inequality for an irreversible process. This is one of the most important equations of thermodynamics. It expresses the influence of irreversibility on the entropy of a system.

For an isolated system, \( \delta Q = 0 \). Thus, in light of Eq. (1.23),
\[
dS_{\text{isolated}} \geq 0. \tag{1.24}
\]
This is the principle of increase of entropy. In accordance with the first law, an isolated system can only assume those states for which the total \( U \) remains
constant. Now according to the second law as expressed by Eq. (1.22) of the states of equal energy, only those states, for which the entropy increases or remains constant, can be attained by the system.

In addition to $U$ and $S$ of a system, several other useful quantities can be defined that are combinations of these and the state variables. One such quantity, already introduced, is $H = U + PV$. There are two combinations of thermodynamic properties involving the entropy being of great utility in thermodynamics, which are the Helmholtz function $F$ and the Gibbs function $G$.

In light of the first law, when a system performs any process, reversible or irreversible, between two equilibrium states, the total work in the process is

$$W + W^* = \Delta U - Q.$$  \hspace{1cm} (1.25)

We now derive expressions for the maximum amount of work that can do when a system undergoes a process between two equilibrium states, for the special case in which the only heat flow is from a single reservoir at a $T$ and the initial and final states are at the same $T$. In light of Eq. (1.24), the sum of the increase in entropy of the system, $\Delta S$, and that of reservoir, $\Delta S_r$, is equal to or greater than zero, namely, $\Delta S + \Delta S_r \geq 0$ and $\Delta S_r = -Q/T$. Hence, $\Delta S - Q/T \geq 0$ and $T \Delta S \geq Q$. As a result, from the first law,

$$\Delta U - T \Delta S = \Delta(U - TS) \leq W + W^*.$$  \hspace{1cm} (1.26)

Let us define a property of the system called Helmholtz function $F$, by the equation

$$F \equiv U - TS,$$  \hspace{1cm} (1.27)

then for two equilibrium states at the same $T$,

$$\Delta F = \Delta U - T \Delta S,$$  \hspace{1cm} (1.28)

and from Eq. (1.26),

$$\Delta F \leq W + W^*.$$  \hspace{1cm} (1.29)

That is, the decrease in $F$ sets an upper limit to the work in any process between two equilibrium states at the same $T$, during which there is a heat flow into the system from a single reservoir at this $T$. If the process is reversible, the equality sign then holds in Eq. (1.29) and the work is a maximum. Against that, when the process is irreversible, the work is less than this maximum.

Equation (1.29) is perfectly general and applies to a system of any nature. The process may be a change of states, or a change of phases, or a chemical reaction.

If both $V$ and $T$ are constants, considering only mechanical work $PdV$, then $W = W^* = 0$ and

$$\Delta F \leq 0, \quad \text{or} \quad F_2 \leq F_1.$$  \hspace{1cm} (1.30)
Take into account next a process under a constant external $P$. $W$ in such a process is $-P \Delta V = -\Delta(PV)$, and from Eq. (1.29),
\[
\Delta F + \Delta(PV) = \Delta(F + PV) \leq W^*.
\] (1.31)

Let us define Gibbs function $G$ as
\[
G \equiv F + PV = U - TS + PV = H - TS.
\] (1.32)

Then for two states at the same $T$ and $P$,
\[
\Delta G \leq W^*.
\] (1.33)

The decrease in $G$ therefore gives an upper limit to the useful work in any process between two equilibrium states at the same $T$ and $P$ where the process is reversible. Because its decrease in such a process equals the maximum energy that can be “freed” and can be the useful work done by a system, the Gibbs function has also been called the free energy of a system. We however shall use the term “Gibbs function” to avoid confusion with the Helmholtz function.

Similar to Eq. (1.30), if the only work is $PdV$, $W^* = 0$ and
\[
\Delta G \leq 0, \quad \text{or} \quad G_2 \leq G_1.
\] (1.34)

That is, in such a process $G$ either remains constant or decreases. Conversely, such a process is possible only if $G_2$ is equal to or less than $G_1$.

### 1.6 General Thermodynamic Relationships [6, 17, 18]

We have defined and used several thermodynamic properties by now. Some of them are directly measurable, but others cannot be measured and must be calculated from data of other properties and quantities, which can be measured. We are now ready to develop some useful general relationships between thermodynamic properties that shall facilitate such calculations. We will restrict our attention to simple systems which require only two independent properties to determine their thermodynamic states. Once the thermodynamic relations are developed for such systems, it is simple to write analogous relations for other simple systems.

We now combine the first and second laws to obtain several important thermodynamic relations. The analytical formulation of the first law, in a differential form, is $dU = \delta Q + \delta W$. The second law states that for a reversible process between two equilibrium states is $\delta Q = TdS$. Also, the work in a reversible process, for a $PVT$ system, is $\delta W = -PdV$. It follows that in any infinitesimal reversible process for a $PVT$ system,
\[
dU = TdS - PdV.
\] (1.35)
This may be used in connection with the definitions of $H$, $F$ and $G$ functions to form three other important relations,

\[ dH = TdS + VdP, \]  
\[ dF = -SdT - PdV, \]  
\[ dG = -SdT + VdP. \]  

Equations (1.35) to (1.38) are four basic relations of properties. They are applicable for any process, reversible or irreversible, between equilibrium states of a simple compressible system with a fixed mass.

A number of useful partial derivative relations can be readily obtained from the four basic relations. They are as follows:

\[ \left( \frac{\partial U}{\partial S} \right)_V = T \quad \text{and} \quad \left( \frac{\partial U}{\partial V} \right)_S = -P, \]  
\[ \left( \frac{\partial H}{\partial S} \right)_P = T \quad \text{and} \quad \left( \frac{\partial H}{\partial P} \right)_S = V, \]  
\[ \left( \frac{\partial F}{\partial T} \right)_V = -S \quad \text{and} \quad \left( \frac{\partial F}{\partial V} \right)_T = -P, \]  
\[ \left( \frac{\partial G}{\partial T} \right)_P = -S \quad \text{and} \quad \left( \frac{\partial G}{\partial P} \right)_T = V. \]

Since $U$, $H$, $F$, and $G$ are all thermodynamic properties and state functions, $dU$, $dH$, $dF$, and $dG$ are exact differentials. Applying these exact conditions to Eqs. (1.35) through (1.38), one obtains

\[ \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V, \]  
\[ \left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P, \]  
\[ \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V, \]  
\[ \left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial V}{\partial T} \right)_P. \]

The above equations are known as the four Maxwell relations. Note that in each of the Maxwell relations the cross product of the differentials has the dimensions of energy. The independent variable in the denominator on one side of an equation is the constant on the other side. They are of great usefulness in the transition of state variables, and particularly in the determination of change in entropy, which are not experimentally measurable, in terms of the measurable properties of $P$, $V$, and $T$. 

The magnetic systems of primary interest in thermodynamics are paramagnetic crystals, whose volume change in a process or \(-PdV\) can be neglected. The only work interaction is due to the magnetization of the material, i.e., \(\delta W^* = H_{\text{mag}}dM\).

A system for which the only reversible work mode is the magnetization of the magnetic material is called a simple magnetic system. This will be taken as an example to illustrate the application of the above equations. The first law for a reversible process in a simple magnetic system is \(dU = \delta Q + H_{\text{mag}}dM\). Combination of this equation and the second law leads to

\[
dU = TdS + H_{\text{mag}}dM.
\]  

Eq. (1.47) is a very basic equation which combines the first and second laws as applied to a simple magnetic system.

It is helpful to define two new properties, the magnetic enthalpy \(H'\) and magnetic Gibbs function \(G'\),

\[
H' = U - H_{\text{mag}}M \quad \text{and} \quad G' = H' - TS = U - TS - H_{\text{mag}}M.
\]

\(F\) takes the usual definition, \(F = U - TS\). Comparing to \(H = U + PV\) in a \(PVT\) system, the equations do have the same form, we can take over all of the equations previously derived for the enthalpy \(H\), replacing \(H\) with \(H'\), \(V\) with \(-M\), and \(P\) with \(H_{\text{mag}}\). From these equations and Eq. (1.47) it follows that

\[
dH' = TdS - MdH_{\text{mag}}, \tag{1.48}
\]

\[
dF' = -SdT + H_{\text{mag}}dM, \tag{1.49}
\]

\[
dG' = -SdT - MdH_{\text{mag}}. \tag{1.50}
\]

Applying the condition of exactness to the four basic relations, Eqs. (1.47) to (1.50), results in the following four Maxwell relations,

\[
\left( \frac{\partial T}{\partial M} \right)_S = \left( \frac{\partial H_{\text{mag}}}{\partial S} \right)_M, \tag{1.51a}
\]

\[
\left( \frac{\partial T}{\partial H_{\text{mag}}} \right)_S = -\left( \frac{\partial M}{\partial S} \right)_{H_{\text{mag}}}, \tag{1.51b}
\]

\[
\left( \frac{\partial S}{\partial M} \right)_T = -\left( \frac{\partial H_{\text{mag}}}{\partial T} \right)_M, \tag{1.51c}
\]

\[
\left( \frac{\partial S}{\partial H_{\text{mag}}} \right)_T = \left( \frac{\partial M}{\partial T} \right)_{H_{\text{mag}}}. \tag{1.51d}
\]

A crystalline metal with the atoms lies on a regular repetitive lattice. When the crystal lattice is perfect, free electrons in the metal are able to pass through it without difficulty. However, there are two factors that generally ruin the perfect arrangement of a crystal lattice and thus give rise to electrical resistance. These are the thermal vibrations of the atoms and the impurities
or imperfections of the metal. As $T$ falls, the thermal vibrations of the lattice atoms decrease, which bring out the decrease of the electrical resistance of metals. Since any real specimen of a metal cannot be perfectly pure and will inevitably contain some impurities, the effect of impurity on electrical resistance is more or less $T$-independent. Thus we can see that impurities and lattice imperfections (point defects, dislocations, interfaces or surfaces) are mainly responsible for the small constant residual resistivity of a metal at very low $T$.

However, many metals exhibit extraordinary behavior. After the residual resistivity of a metal has been reached, when $T$ is further reduced, its electrical resistance suddenly disappears completely. Once a current is introduced in the metal at such low $T$, the current will continue to undergo flow undiminished for an indefinite period of time. This phenomenon was discovered in 1911 by Onnes and was given the name superconductivity. A material having superconductivity at low $T$ is called a superconductor. Since its discovery, the superconductivity has been found in many metallic elements and in a very large number of alloys and compounds, and even in oxides or ceramics.

The superconductivity has many applications. For instance, it can be applied in journal bearings to eliminate friction, in electric motors to reduce internal losses, in electromagnets to obtain very high magnetic fields, and in high-speed computers to form the so-called cryotrons to be used as logic, memory, and comparison elements. There are two kinds of superconductivity, known as type I and type II. Most of those elements exhibiting superconductivity belong to type I, while alloys generally belong to type II. The two types have many properties in common, but there are considerable differences in their magnetic behavior. In 1957 an acceptable fundamental theory of superconductivity was formulated by Bardeen, Cooper, and Schrieffer (BCS theory) when quantum mechanics was applied to the free electrons in a crystal lattice. The complete treatment of the theory is extremely complicated. It requires an advanced knowledge of quantum mechanics and is beyond the scope of this book. It is our intention here to give only a brief descriptive introduction of the thermodynamics of superconductors.

The normal to superconductor transition occurs at a temperature $T_{s,0}$, which depends not only on $P$, but also on the size when the materials are low dimensional. For a strain-free pure bulk metal, $T_{s,0}$ is well defined and can be measured accurately.

Superconductivity can be destroyed by a magnetic field. A magnetic field-strength required to destroy superconductivity in a metal is called a critical or threshold field $H_s$. The uniqueness of $H_s$ at a given $T$ relies on the shape and orientation of the superconductor as well as on any impurity and strain in it. In an ideal case, when a strain-free pure type I superconductor in the shape of a long thin cylinder is placed longitudinally in a uniform magnetic field, the transition between normal and superconductivity is sharp and a unique value of $H_s$ can be obtained at a given $T$, which is only a function of $T$. Figure 1.4(a) shows this dependence of a type I superconductor. It is
observed that $H_s$ curve forms the boundary of superconducting states which divides the $H_s$-$T$ plane into two regions. The area enclosed by $H_s$ curve is the region in which the metal is superconducting. It is normal to go beyond the confines of the curve. $T_{s,0}$ values and the critical field at $T = 0$ K, $H_{s,0}$, for a number of elements are given in Table 1.1.

![Diagram of magnetic field and temperature relationship](image)

**Fig. 1.4** (a) $T$-dependent $H_s$ of a type I superconductor. (b) The effect of zero electrical resistance and zero magnetic induction.

### Table 1.1 The superconducting elements [19]

<table>
<thead>
<tr>
<th>Element</th>
<th>$T_{s,0}$</th>
<th>$H_{s,0}$</th>
<th>Element</th>
<th>$T_{s,0}$</th>
<th>$H_{s,0}$</th>
<th>Element</th>
<th>$T_{s,0}$</th>
<th>$H_{s,0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1.2</td>
<td>$0.79 \times 10^4$</td>
<td>Ir</td>
<td>0.1</td>
<td>$\sim 0.16 \times 10^4$</td>
<td>Ru</td>
<td>0.5</td>
<td>$0.53 \times 10^4$</td>
</tr>
<tr>
<td>Cd</td>
<td>0.5</td>
<td>$0.24 \times 10^4$</td>
<td>La-$\alpha$</td>
<td>4.8</td>
<td></td>
<td>Ta</td>
<td>4.5</td>
<td>$6.6 \times 10^4$</td>
</tr>
<tr>
<td>Ga</td>
<td>1.1</td>
<td>$0.41 \times 10^4$</td>
<td>La-$\beta$</td>
<td>4.9</td>
<td></td>
<td>Tc</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>In</td>
<td>3.4</td>
<td>$2.2 \times 10^4$</td>
<td>Pb</td>
<td>7.2</td>
<td>$6.4 \times 10^4$</td>
<td>Tl</td>
<td>2.4</td>
<td>$1.4 \times 10^4$</td>
</tr>
<tr>
<td>Hg-$\alpha$</td>
<td>4.2</td>
<td>$3.3 \times 10^4$</td>
<td>Sn</td>
<td>3.7</td>
<td>$2.4 \times 10^4$</td>
<td>U-$\alpha$</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Hg-$\beta$</td>
<td>4.0</td>
<td>$2.7 \times 10^4$</td>
<td>Th</td>
<td>1.4</td>
<td>$1.3 \times 10^4$</td>
<td>U-$\beta$</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.9</td>
<td></td>
<td>Ti</td>
<td>0.4</td>
<td></td>
<td>V</td>
<td>5.3</td>
<td>Type II</td>
</tr>
<tr>
<td>Nb</td>
<td>9.3</td>
<td>Type II</td>
<td>W</td>
<td>0.01</td>
<td></td>
<td>Zn</td>
<td>0.9</td>
<td>$0.42 \times 10^4$</td>
</tr>
<tr>
<td>Os</td>
<td>0.7</td>
<td>$\sim 0.5 \times 10^4$</td>
<td>Zr</td>
<td>0.8</td>
<td>$0.437 \times 10^4$</td>
<td>Re</td>
<td>1.7</td>
<td>$1.6 \times 10^4$</td>
</tr>
</tbody>
</table>

Figure 1.4(a) reveals that every critical field curve has a negative slope, which increases in magnitude from zero at 0 K to a finite value at $T_0$. These curves may be approximated by a parabolic equation of the form
In addition to the disappearance of electrical resistivity, a superconducting metal also shows a magnetic effect – the disappearance of magnetic induction. The phenomenon of zero magnetic induction was discovered by Meissner and Ochsenfeld in 1933 and is now commonly known as the Meissner effect. Its meaning can be understood by considering a type I superconducting metal going through a few processes as depicted in Fig. 1.4(a). The specimen is first cooled at zero magnetic field from a normal state \( a \) to a superconducting state \( b \), and then is magnetized at constant \( T \) from state \( b \) to state \( c \), which is well below the critical field curve. When the magnetic field is applied to the specimen in superconducting states, persistent currents induced on the surface of the specimen prevent the field from penetrating the metal. Thus, as illustrated in Fig. 1.4(b), at state \( c \) the magnetic lines of forces are bulging around the specimen. When the specimen is heated in a constant \( H_s \) from state \( c \) to state \( d \), where \( H_s \) curve is passed, the persistent current on its surface dies out and magnetic flux penetrates into it. Thus, as illustrated in Fig. 1.4(b), \( H_s \) has uniformly penetrated the metal at state \( d \) since the metal is now in a normal state and is virtually nonmagnetic. The fact that the magnetic field is expelled from the metal when it becomes superconducting implies not only infinite electrical conductivity, but also perfect diamagnetism. This is the essence of the Meissner effect.

As a further illustration of the magnetic nature of superconductivity, let us consider the variations of the magnetic induction \( B \) and the magnetization \( \mu_v \) of a type I superconductor as \( H_{\text{mag}} \) is increased isothermally across the critical field. In general, \( B = \mu_0 (H_{\text{mag}} + \mu_v) \). When the metal is in superconducting phase, we have

\[
B = 0, \quad \text{and} \quad \mu_v = -H_{\text{mag}},
\]

whereas beyond \( H_s \) corresponding to the given \( T \), the metal is normal. Since normal metals (excluding ferromagnetic metals, such as Fe) are virtually nonmagnetic, it follows

\[
\mu_v = 0, \quad \text{and} \quad B = \mu_0 H_{\text{mag}}.
\]

There is another property of a metal, which changes abruptly during transitions from normal to superconductivity. As we know, conduction heat transfer in a metal is mainly due to the mobility of free electrons. However, at a superconducting state the free electrons of a metal no longer interact with the lattice in such a way that the electrons can pick up heat energy from one part of the metal and deliver it to another part. Therefore when a metal becomes superconducting, its thermal conductivity decreases in general. At \( T << T_{s,0} \), the decrease in thermal conductivity is abrupt at the crossing of the critical field curve. Since superconductivity can be destroyed by the application of a magnetic field, the thermal conductivity of a superconductor can be easily controlled by means of a magnetic field. This is the basic principle for a thermal valve.
A type I superconducting system at any values of $H_{\text{mag}}$ and $T$ within the superconducting region has a strictly fixed state and is independent of how the system got there. Hence a type I superconductor may be considered as a thermodynamic system whose equilibrium states can be described by a few thermodynamic properties, and the transitions between normal and superconducting states are reversible.

As plotted in Fig. 1.4, below $H_s$ curve the system is in the superconducting phase. Otherwise, the normal phase is present. $H_s$ curve itself is the equilibrium line for the phase coexistence. In general, the transition between normal and superconducting phases, taking place at constant $T$ and $H_s$, involves a finite latent heat, denoting a first order phase transition. We now derive the equation for the latent heat as functions of $T$ and $H_s$. According to Eq. (1.50), the differential of the magnetic Gibbs function is given by $dG = -SdT - M dH_{\text{mag}}$. At $T = \text{constant}$ and $H_{\text{mag}} = H_s = \text{constant}$, we must have $dG = 0$, or $G''(n) = G''(s)$, where the superscripts $(n)$ and $(s)$ denote respectively normal and superconducting phases. When $T$ and $H_s$ are increased to $T + dT$ and $H_s + dH_s$ respectively, $G''(n) + dG''(n) = G''(s) + dG''(s)$, or $dG''(n) = dG''(s)$. Applying Eq. (1.50), we obtain $-S(n) dT - M(n) dH_s = -S(s) dT - M(s) dH_s$. Therefore, $-dH_s/dT = (S(n) - S(s))/(M(n) - M(s))$. In light of Eqs. (1.52) and (1.53), $M(n) = \mu_0 V \mu^0_v(n) = 0$ and $M(s) = \mu_0 V \mu^0_v(s) = -\mu_0 V H_s$. It follows

$$\Delta S_{\text{sn}} = S(n) - S(s) = -\mu_0 V H_s \frac{dH_s}{dT}. \tag{1.54}$$

Now since $\Delta H_s = T(S(n) - S(s))$ = latent heat, we obtain finally

$$\Delta H_{\text{sn}} = -\mu_0 VT H_s \frac{dH_s}{dT}. \tag{1.55}$$

Since $dH_s/dT$ is always negative, we see from Eq. (1.54) that $S(n) > S(s)$. Since entropy is physically an index of orderliness, we conclude that more orders exist in the superconducting than in the normal phase. From Eq. (1.55) we see that $\Delta H_{s,0} = 0$ at the two extremes of $H_s$ curve, i.e., $dH_s/dT$ at $T = 0$, and $H_s = 0$ at $T = T_{s,0}$. Between them, $\Delta H_{\text{sn}} > 0$, indicating that heat addition is required in changing from superconducting to normal phase.

Since the transition between normal and superconducting phases takes place at $T_{s,0}$ without latent heat evolution in the absence of a magnetic field while heat capacity shows a discontinuity at $T_{s,0}$, this phase transition is obviously of the second order.

There are some useful relationships concerning $C$ and $H_s$. With simple mathematical treatment of Eq. (1.54), we obtain $TdS(n)/dT - TdS(s)/dT = -\mu_0 VT d(H_s dH_s/dT)/dT$. Since $C = T dS/dT$, it reads

$$C(s) - C(n) = -\mu_0 VT \frac{d}{dT} \left( H_s \frac{dH_s}{dT} \right). \tag{1.56}$$
or \( C^{(s)} - C^{(n)} = \mu_0 VT (dH_s/dT)^2 + \mu_0 VTH_s d^2H_s/dT^2 \). Equation (1.56) can be used to determine \( C^{(s)} - C^{(n)} \) from measurements of magnetic properties for an ideal type I superconductor. At \( T = T_{s,0} \) and \( H_s = 0 \), Eq. (1.56) reduces to

\[
\left( \frac{dH_s}{dT} \right)^2_{T=T_{s,0}} = \frac{1}{\mu_0 VT_{s,0}} (C^{(s)} - C^{(n)})_{T=T_{s,0}},
\]

(1.57)

This equation could be utilized to determine the slope of \( H_s \) curve at \( T_{s,0} \) from measurements on \( C \). Conversely, the magnitude of \( C \) jump at \( T_{s,0} \) decides the slope of \( H_s \) curve. Integrating Eq. (1.56) from \( T = 0 \) and \( H_s = H_{s,0} \) to \( T = T_{s,0} \) and \( H_s = 0 \) along \( H_s \) curve, there is

\[
\int_0^{T_{s,0}} (C^{(s)} - C^{(n)})dT = \mu_0 V \int_{H_s}^0 T \cdot \left( \frac{dH_s}{dT} \right) _{T=H_{s,0}}^{T_{s,0}} - \mu_0 V \int_{H_{s,0}}^{H_s} H_s \frac{dH_s}{dT}
\]

where the method of integration has been used in part. Now, since at \( T = T_{s,0}, H_s = 0 \), the first term in the last expression is zero, and therefore,

\[
\int_0^{T_{s,0}} (C^{(s)} - C^{(n)})dT = \frac{1}{2} \mu_0 V H_{s,0}^2, \quad \text{or} \quad H_{s,0}^2 = \frac{2}{\mu_0 V} \int_0^{T_{s,0}} (C^{(s)} - C^{(n)})dT
\]

which is useful to determine \( H_{s,0} \) from heat capacity measurements.

Until 1986, physicists had believed that BCS theory forbade superconductivity at \( T > 30 \text{ K} \). In that year, Bednorz and Müller discovered superconductivity in a lanthanum-based cuprate perovskite material, which had a \( T_{s,0} \) of 35 K without a magnetic field [20]. Particularly, the lanthanum barium copper oxides, an oxygen deficient pervoskite-related material, are proved to be promising. In 1987, Bednorz and Müller were jointly awarded the Nobel Prize in Physics for this work. Shortly after that, Chu and his co-workers found that replacing La with Y, often abbreviated to YBCO, raised \( T_{s,0} \) to 93 K [21]. YBCO compound with the formula \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) is a famous high-temperature superconductor because from a practical perspective, it was the first material to achieve superconductivity above \( T_b \) of \( \text{N}_2 \) of 77 K at atmospheric pressure. Their work led to a rapid succession of new high temperature superconducting materials, ushering a new era in the study of superconductivity. However, although many other cuprate superconductors have since been discovered, the theory of superconductivity in these materials is one of the major outstanding challenges of theoretical condensed matter physics.

Magnesium diboride \( (\text{MgB}_2) \) is another inexpensive and useful superconducting material. Although this material was first synthesized in 1953, its superconductivity had not been discovered until 2001 [22]. Magnetization and resistivity measurements established a \( T_{s,0} \) of 39 K, which was believed to be the highest yet determined for non-copper-oxide bulk superconductors.
Though it is generally believed to be a conventional (phonon-mediated) superconductor, MgB$_2$ is rather an unusual one. In fact, it is a multi-band superconductor, that is, each Fermi surface has different superconducting energy gaps. This differs from usual theories of phonon-mediated superconductivity, which assume that all electrons behave in the same manner. Moreover, MgB$_2$ was regarded as behaving more like a low temperature metallic superconductor than a high temperature cuprate superconductor.

Very recently, researches have discovered a new family of high temperature superconductors. In 2008, Hosono and his colleagues reported that lanthanum oxygen fluorine iron arsenide LaO$_{1-x}$F$_x$FeAs becomes a superconductor at $2.6 \times 10^6$ K [23, 24]. Thereafter, Chen and his colleagues found that samarium oxygen fluorine iron arsenide (SmO$_{1-x}$F$_x$FeAs) goes superconducting at 43 K [25]. Physicists consider the discovery of the new iron-and-arsenic compounds as a major advance, which are the only other high-temperature superconductors differing from the copper-and-oxygen compounds found in 1986. The mechanisms of the new superconductors are believed to be different from those of the old ones, since the latter evolves from a state with one electron per copper ion, whereas the former evolves from a state with two electrons per iron ion. Nowadays, the new materials are generating intense interest to synthesize higher quality samples consisting of a single pristine crystal in the next step.

1.7 Third Law of Thermodynamics [6, 17, 18]

A basic law of thermodynamics was born from the attempt to calculate equilibrium constants of chemical reactions entirely from thermal data (i.e., $H$ and $C_{P,m}$). What has come to be known as the third law of thermodynamics had its origin in the Nernst heat theorem. Nernst noted from the experimental results by Thomsen and Berthelot, and by careful experiments with galvanic cells. In the experiments, $\Delta G$ in a reaction generally approached $\Delta H$ more closely as $T$ was reduced, even at quite high $T$. In 1906, he therefore proposed a general principle that as $T \to 0$, not only did $\Delta G$ and $\Delta H$ approach equality, but their rates of change with $T$ approached zero. That is,

$$\lim_{T \to 0} \left( \frac{\partial \Delta G}{\partial T} \right)_P = 0, \quad \lim_{T \to 0} \left( \frac{\partial \Delta H}{\partial T} \right)_P = 0.$$  \hspace{1cm} (1.58)

In geometric terms this means that the graphs of $\Delta G$ and $\Delta H$ as a function of $T$ both have the same horizontal tangent at $T = 0$ as shown in Fig. 1.5.

The first of Eq. (1.58) can be rewritten as

$$\lim_{T \to 0} \left( \frac{\partial (G_2 - G_1)}{\partial T} \right)_P = \lim_{T \to 0} \left[ \left( \frac{\partial G_2}{\partial T} \right)_P - \left( \frac{\partial G_1}{\partial T} \right)_P \right] = 0.$$  \hspace{1cm} (1.59)
Since \((\partial G/\partial T)_P = -S\),
\[
\lim_{T\to 0} (S_1 - S_2) = 0.
\] (1.60)

This is the Nernst heat theorem, which states that in the neighborhood of absolute zero, all reactions in a liquid or solid in internal equilibrium take place without change in entropy.

Planck, in 1911, made a further hypothesis that not only the entropy difference vanishes as \(T \to 0\), but also that the entropy of every solid or liquid substance in internal equilibrium at absolute zero is itself zero, that is,
\[
\lim_{T \to 0} S = 0.
\] (1.61)

This is named the third law of thermodynamics. If the substance is heated reversibly at constant \(V\) or \(P\) from \(T = 0\) to \(T = T\), its entropy at \(T\) is
\[
S(V,T) = \int_0^T C_V \frac{dT}{T}, \quad S(P,T) = \int_0^T C_P \frac{dT}{T}. \] (1.62)

Because entropy changes near room temperature are often needed in thermodynamic calculations, the integral of Eq. (1.62) has been evaluated for many substances at 298 K, which is generally called the “standard” entropies. The form in Eq. (1.62) assumes that no phase changes take place between 0 K and \(T\). If there are phase transitions, such as solid to liquid and liquid to gaseous transitions in the region of 0 K and \(T\), they must be considered in the integration,
\[
S(P,T) = \int_0^{T_m} C_P \frac{dT}{T} + \frac{\Delta H_m}{T_m} + \int_{T_m}^{T_b} C_P \frac{dT}{T} + \frac{\Delta H_b}{T_b} + \int_{T_b}^T C_P \frac{dT}{T}. \] (1.63)

where \(\Delta H_m\) and \(\Delta H_b\) are the molar enthalpies of melting and boiling, respectively, and \(T_m\) and \(T_b\) are the corresponding melting points.

Now since the third law asserts that the entropy of any substance must be finite or zero at 0 K, it follows that the entropy of a substance must be finite at any finite \(T\). Consequently, from Eq. (1.62) we conclude that
\[
\lim_{T \to 0} C_V = \lim_{T \to 0} C_P = 0.
\] However, \(C_P/T = (\partial S/\partial T)_P\) may in fact diverge as
$T$ approaches 0 K. The Nernst theorem implies that the change in entropy is zero in any process at 0 K. For example,

$$\lim_{T \to 0} \left( \frac{\partial S}{\partial P} \right)_T = \lim_{T \to 0} \left( \frac{\partial S}{\partial V} \right)_T = 0.$$  \hspace{1cm} (1.64)

The derivatives of many thermodynamic properties are related to the derivatives of the entropy through the Maxwell relations. Using the relations, we obtain

$$\lim_{T \to 0} \left( \frac{\partial V}{\partial T} \right)_P = \lim_{T \to 0} \left( \frac{\partial P}{\partial T} \right)_V = 0.$$  \hspace{1cm} (1.65)

Since coefficient of thermal expansion $\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$ and $V$ remains finite as $T \to 0$, we can also write the compressibility $\beta$ as

$$\lim_{T \to 0} \beta = 0.$$  \hspace{1cm} (1.66)

The third law also implies that it is impossible to reduce $T$ of a system to 0 K in any finite number of operations.

References

16 http://en.wikipedia.org/wiki/Thermodynamic_process
23 Kamihara Y, Watanabe T, Hirano M, Hosono H. Iron-based layered superconductor La[O$_{1-x}$F$_x$]FeAs ($x = 0.05 - 0.12$) with $T_c = 26$ K. J. Am. Chem. Soc., 130, 3296-3297 (2008)