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1 Why Study Thermodynamics?

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1.1 THE POWER AND BREADTH OF THERMODYNAMICS

A survey of undergraduate curricula in materials science and engineering showed that every program requires a core course in thermodynamics. In more than 90% of those programs, the course is taught within the department. Most graduate programs have one or more courses in the subject. Evidently there is widespread agreement that this subject is a central one in materials science and engineering. The same statement can be made for programs in chemical engineering and chemistry and, perhaps to a lesser extent, physics.

Why?

Five primary reasons:

1. Thermodynamics is pervasive.
2. Thermodynamics is comprehensive.
3. Thermodynamics is established.
4. Thermodynamics provides the basis for organizing information about how matter behaves.
5. Thermodynamics enables the generation of maps of equilibrium states that can be used to answer a prodigious range of questions of practical importance in science and industry.

Thermodynamics is pervasive; it applies to every volume element in every system at every instant in time. How pervasive can you get?

Thermodynamics is comprehensive. The apparatus is capable of handling the most complex kinds of:

Systems: metals, ceramics, polymers, composites, solids, liquids, gases, solutions, crystals with defects

Applications: structural materials, electronic materials, corrosion-resistant materials, nuclear materials, biomaterials, nanomaterials

Influences: thermal, mechanical, chemical, interfacial, electrical, magnetic

Thermodynamics is established. J. Willard Gibbs essentially completed the apparatus of phenomenological thermodynamics in 1883 in his classic paper, *On the Equilibrium of Heterogeneous Substances*. The scientific and technological explosion of more than a century has not required a significant modification of Gibbs' apparatus.

Thermodynamics provides the basis for organizing information about how matter behaves. Thermodynamics identifies the properties of systems that are scientifically and technologically important in a wide range of applications. It identifies the subset of these properties that are sufficient to compute all the others. These are the properties that are measured in the thermochemistry laboratories of the world and have been accumulating in the databases of the world since Gibbs' time. The apparatus then provides relationships between these database properties and the functions that are crucial in predicting the behavior of matter.

Thermodynamics enables the generation of maps of equilibrium states for this broad spectrum of systems and influences. A variety of species of such maps are widely used in science and industry to answer real-world questions about the behavior of matter.

Will cadmium melt at 545°C?

If the temperature of the air outside drops eight more degrees, will it get foggy?

If I heat this Nb-Ti-Al alloy in air to 1100°C, will it oxidize?

Can this polymer solvent dissolve 25% PMMA at room temperature without phase separating?

How can I prevent the oxidation of silicon carbide when I hot press it at 1350°C?

How can I control the defect concentration in this fuel cell membrane?

What source temperatures should I use to codeposit a 40 to 60 Ge-Si thin film from the vapor phase?

Will silicon carbide fibers be stable in an aluminum nitride matrix at 1300°C?

Will titanium corrode in seawater?

Finally, a warning: thermodynamics is a very rational subject. The logic is largely linear. C follows from B, which follows from A. Nonetheless the predictions of thermodynamics are full of surprises. Accordingly, intuition applied to thermodynamics can be dangerous and misleading, particularly for the uninitiated. Students for which intuition plays an important role in their learning processes may

have difficulty with thermodynamics. It is important to understand the laws and strategies of thermodynamics and let the logic lead where it will.

1.2 THE GENERIC QUESTION ADDRESSED BY THERMODYNAMICS

The questions in the preceding paragraph are all forms of a generic question which thermodynamics addresses (see Figure 1.1): "if I take System A in Surroundings I and put it into Surroundings II, what will happen?" Rudimentary thermodynamics concepts implicit in this question include:

System, which is the collection of matter whose behavior is the focus of the question.

Surroundings, which is the matter in the vicinity of the system that is altered because it interacts with it.

Boundary, implicit in the concept of a system and its surroundings, which may limit the kinds of exchanges that can occur between the two.

Properties, required in the definition of the condition of a system and its surroundings.

As an example of this generic scenario, consider a block of cadmium sitting on a laboratory bench so that its initial condition is ambient pressure and temperature (nominally 1 atm and 25°C). It is picked up with a pair of tongs and placed in a furnace, which has its temperature controlled at 545°C.

In Figure 1.1, System A is the piece of solid cadmium. Surroundings I is the ambient pressure and temperature of the laboratory. Surroundings II is the atmosphere in the furnace also at ambient pressure but a temperature of 545°C. System A experiences a change in surroundings when it is placed in the furnace. As a result, System A begins to change its condition toward a final state B, which is in equilibrium with this new Surroundings II. It is necessary to consult a thermodynamics database that has information about cadmium to determine that the melting point of cadmium is 321°C and the vaporization temperature is 767°C. Thus, the final equilibrium state in its new surroundings is liquid cadmium.

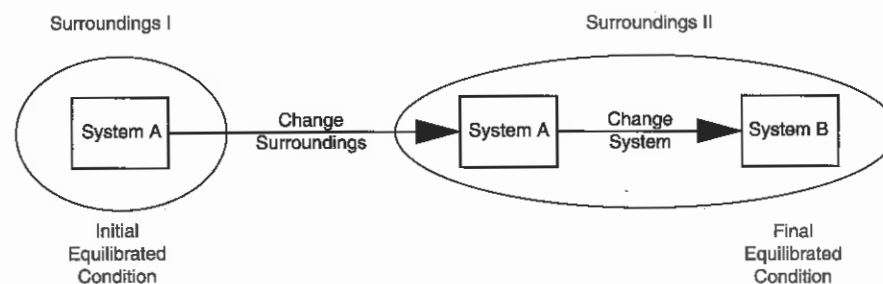


FIGURE 1.1 The generic question addressed in thermodynamics.

What happens? The cadmium melts. The process involved in this change is melting, a phase transformation in which the crystalline structure of solid cadmium is converted to a structure that is liquid. Pockets of the liquid phase nucleate, forming a solid/liquid interface. The motion of this interface toward the solid phase increases the amount of liquid at the expense of the solid phase until there is no solid phase left.

Practically speaking, a number of issues that are ignored in this simple description of the process also need to be addressed. Since the cadmium will melt, it has to be placed in a container, e.g., a crucible, before it is put in the furnace. Will the container react chemically with the cadmium? Also, cadmium vapor will form over the liquid. How high will the vapor pressure become? Cadmium vapor is toxic, so significant precautions will have to be taken to contain the sample and its vapor. If the ambient atmosphere is air, will cadmium oxide (or other compounds) form? Evidently a comprehensive answer to the question, "what will happen?" requires answers to all of these questions. Thermodynamics has the power to address all of these issues.

The scenario shown in Figure 1.1 can be used to frame a variety of rearrangements of the generic question:

What Surroundings II must be provided to convert System A into a specific version of System B? (For example, what range of temperatures can I use to convert BCC iron to FCC iron?)

What Surroundings II must be used to prevent the conversion of System A into a specific System B? What surroundings must be avoided? (For example, what range of furnace atmosphere compositions must be used to avoid the oxidation of a set of turbine blades during heat treatment?)

The apparatus of thermodynamics provides the answer to these kinds of questions by providing the basis for determining the equilibrium state of any system in any surroundings.

1.3 THERMODYNAMICS IS LIMITED TO SYSTEMS IN EQUILIBRIUM

Thermodynamics is limited to the description of systems that are in equilibrium with their surroundings. It provides the basis for predicting what the properties of an equilibrated system will be as a function of the content of the system and the characteristics of its surroundings. Thermodynamics does not permit the prediction of the step-by-step time-dependent evolution of a system toward equilibrium. That level of description of the behavior of matter, which is contained in a formalism called the thermodynamics of irreversible processes, requires the solution of sets of simultaneous partial differential equations. Implementation of this time-dependent description requires a great deal more information about the system than does the description of its equilibrium state in given surroundings. Irreversible thermodynamics is beyond the scope of this text. However, equilibrium thermodynamics,

which is the subject of this text, provides the context within which these time-dependent processes occur.

How then can equilibrium thermodynamics be usefully applied in answering the question, "what will happen?"

System A has some set of properties when it was in Surroundings I. These are the initial properties of the system when it is placed in Surroundings II. Thermodynamics predicts what the state of this system will be when it comes to equilibrium with its new Surroundings, II. This provides a basis for deducing what processes must occur to change the system from its initial condition, inherited from Surroundings I to its equilibrium state in Surroundings II.

Thermodynamics provides not only the equilibrium state in such cases, but also some measure of how far the system is from the equilibrium state. These thermodynamic measures, perhaps misleadingly labeled "driving forces" in kinetic descriptions of processes, play a central role in the more sophisticated attempts to describe the sequence of states through which the system passes as it moves toward equilibrium and its rate of progress through that sequence.

The real utility of thermodynamics lies in its ability to predict whole patterns of behavior for a range of systems in a range of surroundings. These patterns are conveniently presented in the form of maps of equilibrium states. Thermodynamics produces a variety of such maps for different classes of systems operating in appropriate types of surroundings. Generation of these maps is a main topic of this text. Such a map provides an ability to answer the question, "what will happen?" for any combinations of systems and surroundings encompassed by the map.

Figure 1.2 is a sketch of such a map for a familiar substance, water. The system under consideration (System A) is some fixed quantity of the molecular specie H_2O . It is known that this specie can exhibit a number of structures (phases), depending upon its surroundings: solid, liquid and vapor (ice, water and steam or water vapor). (Ice can exist in a number of different crystalline forms but these occur outside the window of temperature and pressure represented here.) The condition of the surroundings that may be considered as imposed upon the system is specified

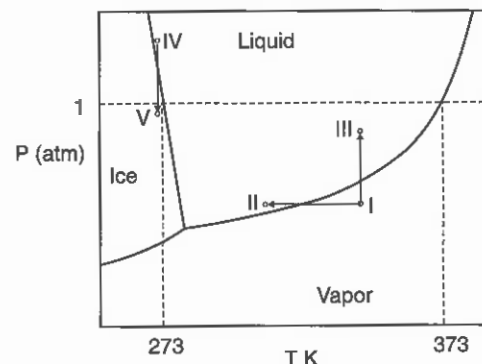


FIGURE 1.2 Sketch of a unary phase diagram for water. The negative slope of the solid-liquid line is real, but exaggerated to illustrate a point in the text.

by two variables: pressure, P and temperature, T . The map, called a phase diagram, is a display of the equilibrium state of this system for any selected state of the surroundings. The domain labeled solid is the range of surrounding conditions, temperatures and pressures, for which the final equilibrium state of the structure is solid water, i.e., ice. The other two areas labeled liquid and vapor are the ranges of combinations of P and T in the surroundings for which the equilibrium state is, respectively, liquid and vapor.

To illustrate how this diagram addresses the “what happens?” question posed above, suppose that a quantity of specie H_2O (System A) is initially at a temperature of 70°C with a vapor pressure of 0.62 atm, point I in Figure 1.2. The map reports that in these “Surroundings I” System A is in the vapor state, i.e., the H_2O exists as water vapor. Suppose the temperature drops to 30°C without changing the pressure in the surroundings. This “Surroundings II” is represented by the point II in Figure 1.2. Point II lies within the domain for which the equilibrium state is liquid water. What happens? Droplets of liquid begin to form and grow (dew perhaps evolving into rain, depending upon a host of other conditions). There is a nucleation process in which collisions of water molecules form tiny clusters that eventually attain a critical size of the liquid phase for growth. These grow by further collisions with molecules in the vapor and drop to the bottom of the container to form the liquid phase in bulk. Sophisticated theories for each of these kinetic processes (nucleation and growth) predict the rate at which they may happen, the dispersion of droplet sizes, and identify the kinetic and thermodynamic variables that control these processes.

A similar sequence of events would occur if System A in Surroundings I were contained in a cylinder with a piston and a force applied to move the piston to increase the vapor pressure to create a new Surroundings III, point III in Figure 1.2. This state also lies in the domain of liquid water on the map. Again, water droplets will nucleate and grow and eventually coalesce to form the bulk liquid. The resulting liquid occupies a small fraction of the precursor vapor phase so that the piston will rapidly drop to nearly the bottom of the cylinder when the vapor condenses.

A container of liquid water initially in Surroundings IV (point IV in Figure 1.2) would contain liquid water at this temperature and pressure. If the pressure is relieved so that it drops to 1 atm at the same temperature (point V), what happens? The equilibrium state in Surroundings V is solid H_2O . You may have observed that, when the top is popped off a bottle of liquid cola that has been in the freezer for a while (and which is under pressure from the dissolved gases that make it effervesce) the liquid cola may suddenly freeze completely. This situation leads to the consideration of the process of nucleation of ice crystals followed by their growth.

Figure 1.3 is a sketch of the map of the domains of stability of the phases for the element molybdenum. Like H_2O , molybdenum exhibits three phase forms, solid, liquid and vapor. The maps in Figure 1.2 and Figure 1.3 are qualitatively similar, but the quantitative differences are spectacular. At 1 atm pressure liquid water is stable between 273 and 373 K. Under 1 atmosphere pressure the range of stability of liquid molybdenum is from 2980 to 4912 K. This huge difference in behavior reflects the nature of the bonds that hold water molecules together in comparison to those that act between molybdenum atoms.

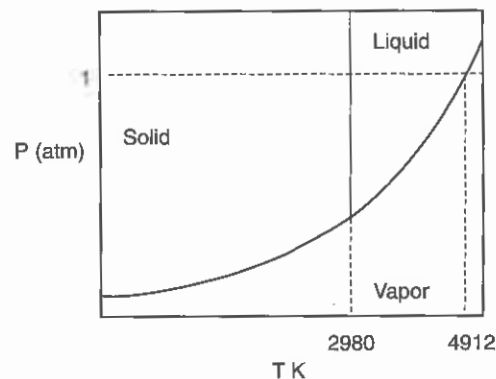


FIGURE 1.3 Sketch of a unary phase diagram for molybdenum. The diagram is qualitatively similar to that for water, but the quantitative differences are enormous.

The thermodynamic equations underlying the calculation of these two maps are identical in form. Thermodynamics provides the basis for defining and identifying the properties of each phase that must be determined in the laboratory in order to calculate these two maps. A database, laboriously developed over time, that collects and summarizes values for these properties for the elements in the periodic table and for many compounds, provides the experimental information specific to each specie that must be used in the computation of its map. Strategies, also derived from thermodynamic principles, are then applied to compute the map from its database.

Thus thermodynamics provides the definitions of the properties that must be measured to form the database for a phase diagram map for systems that contain one chemical component. The discipline also provides the principles and strategies needed to produce quantitative maps of equilibrium states from this database information.

1.4 THE THERMODYNAMIC BASIS FOR EQUILIBRIUM MAPS

Figure 1.4 provides a summary of the component parts of thermodynamics and how they fit together to produce maps that are ultimately used to answer practical questions. The concepts and connections in this figure provide a very useful basis for understanding the rudiments of how thermodynamics works and will be referred to frequently as the arguments develop in the text.

The content of the field is contained in a few principles that are applied through a few strategies.

1.4.1 THE PRINCIPLES

In phenomenological thermodynamics each system is a structureless glop that is endowed with properties. As a first step, properties that make thermodynamics work must be identified and defined, such as temperature, pressure, composition,

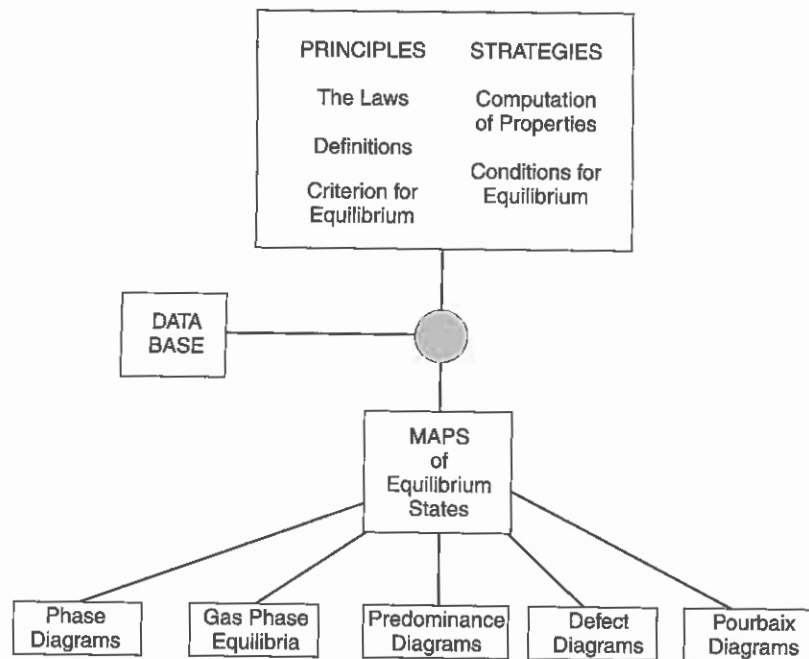


FIGURE 1.4 Representation of the structure of thermodynamics illustrating how the component parts of thermodynamics join together to generate maps of equilibrium states.

heat capacity, coefficient of thermal expansion and compressibility, entropy, and various measures of the energy of the system. Definitions of properties are introduced throughout the text as new system and surroundings variables are introduced.

The central principles of thermodynamics are the three laws that are described in Chapter 3.

The general criterion for equilibrium, deduced from the second law, is developed in Chapter 5. Since a primary goal of the text is the exposition of equilibrium states that matter will exhibit, there must be a basis for determining when a system is in equilibrium.

1.4.2 THE STRATEGIES

A general strategy for calculating all of the thermodynamic properties of a system from a minimum list of database properties is developed in Chapter 4.

The conditions for equilibrium are a set of equations between properties of the system that must be satisfied when the system is in equilibrium. These equations are the basis for calculating maps of equilibrium states from database information. The list of equilibrium equations expands as the nature of the system under study grows more complex, requiring additional variables in the description of its state. This strategy is first applied to a simple system in Chapter 5. The same strategy for deriving conditions for equilibrium is applied repeatedly in

the remaining chapters of the text as systems of increasing variability and complexity are treated.

1.4.3 DATABASES

Thermodynamics identifies the minimum information set that must be obtained to compute the properties of a system. The list of properties in this minimum set expands as the system under consideration exhibits more variables. For example, there are no composition variables in a one-component (unary) system; heat capacity, coefficients of thermal expansion and compressibility are sufficient to compute the rest of the properties of such a simple system (Chapter 4). Additional information is required to treat systems that exhibit more than one phase, e.g., solid plus liquid, (Chapter 7). Treatment of multicomponent system requires additional chemical variables with associated required database properties (Chapter 8). Further information is required to treat additional phases that a multicomponent system may exhibit (Chapters 9 and 10). Systems capable of chemical reactions (Chapter 11) require yet another kind of data.

The vast scientific literature continues to expand, and information gleaned from the work of thousands of experimenters over decades continues to accumulate, be analyzed and assessed as it passes into the thermochemical databases of the world. The principles and strategies of thermodynamics render that data into the practical form of equilibrium maps. The map provides answers to "what will happen?" questions.

1.4.4 MAPS OF EQUILIBRIUM STATES

Examples of the maps shown in the bottom row of Figure 1.4 are described briefly below.

1. The phase diagram shown in Figure 1.5 is for the silver–magnesium system at 1 atm pressure. A point in the diagram represents the equilibrium structure of a particular Ag–Mg composition at a particular temperature. The vapor phase is stable above the range of temperature presented in this diagram. This map may be used to answer "what will happen?" questions similar to those illustrated in Figure 1.2 and Figure 1.3.
2. The equilibrium gas composition map shown in Figure 1.6 displays the equilibrium composition (expressed as its partial pressure in the mixture) of one of the components in a mixture of gases, in this case, the molecule O_2 , as a function of the overall chemistry of the system reported by the relative quantities of the elements carbon, hydrogen and oxygen that make up the system. The lines on the diagram are calculated from a database reporting properties of the chemical reactions involved in forming the molecular components that can be made by combining these three elements. These "iso-oxygen contours" report the locus of points that will provide a fixed partial pressure of oxygen for the temperature

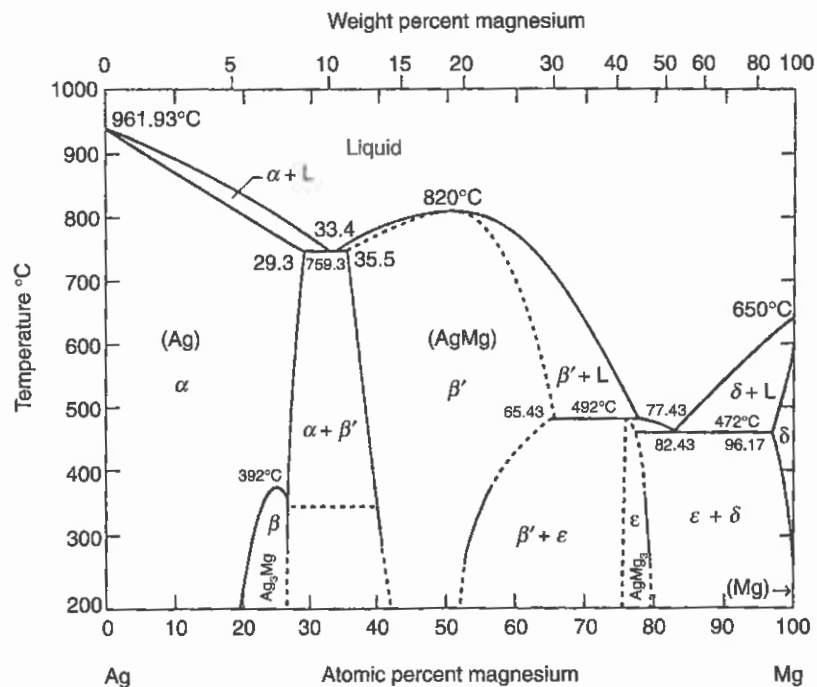


FIGURE 1.5 Phase diagram for the silver-magnesium system at 1 atm pressure.

of the diagram. This kind of map provides the basis for the design of furnace atmospheres with controlled chemistry for heat treatment, coating formation, vapor deposition and stoichiometry control.

- The predominance diagram shown in Figure 1.7 is computed from a thermodynamic database that provides information about the chemical reactions that form the compounds displayed on the diagram. Regions on this diagram represent domains of predominance of each compound considered in the database relative to all the others in the system. The information is presented at a fixed temperature as a function of the chemistry of the gas atmosphere that forms its surroundings. Predominance diagrams provide a reasonable approximation to the phase diagram in such complex systems and require significantly less data. These maps may be used in conjunction with a gas composition map to determine the range of elemental composition of the atmosphere necessary to produce each compound.
- An example of an equilibrium crystal defect diagram is shown in Figure 1.8. A database providing thermodynamic property changes associated with the formation of defects (vacancies, interstitials, anti-site defects, etc.) in compound crystals permits calculation of the concentration of each class of defect as a function of the departure of the composition of the compound crystal from its stoichiometric formula.

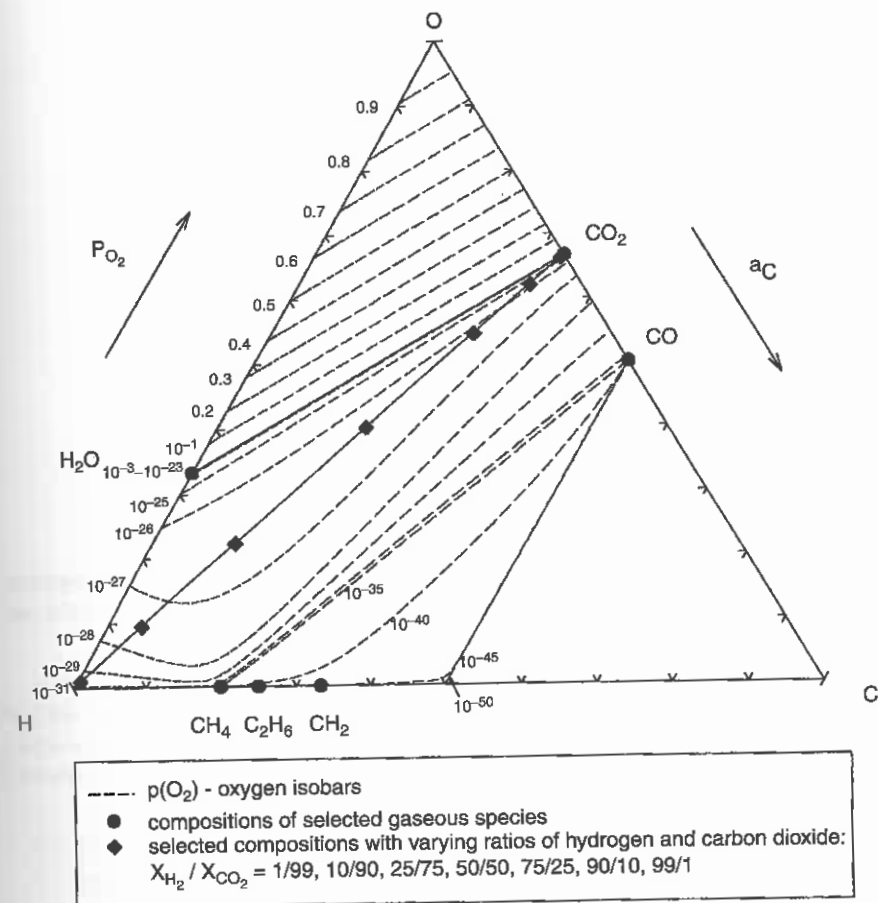


FIGURE 1.6 An equilibrium gas composition map for a gas mixture containing carbon, hydrogen and oxygen displays contours of constant partial pressure of one of the components (in this case the oxygen molecule, P_{O_2}) as a function of the elemental content of the gas mixture.

This departure can be controlled by manipulating the chemistry of the gas atmosphere with which the compound is equilibrated. Manipulation of this defect chemistry has important applications in microelectronic devices, nuclear fuel pellets, sensors, fuel cells, batteries and other devices, which lie at the interface between chemistry and electronic behavior.

- Figure 1.9 illustrates a Pourbaix electrochemical diagram named after M. Pourbaix who devised the diagram and popularized its use in the analysis of corrosion behavior. The diagram shown illustrates the behavior of copper in aqueous solutions in the presence of an applied electromotive force. This form of predominance diagram is computed with procedures that mimic those needed in evaluating the more

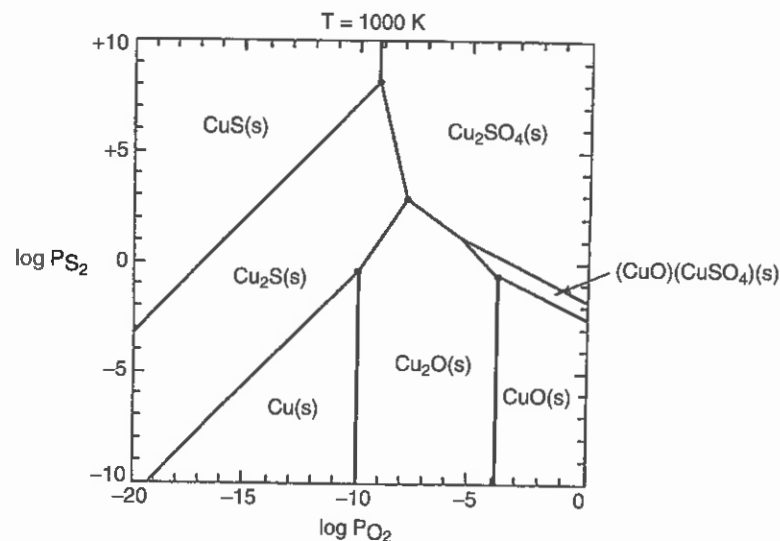


FIGURE 1.7 Predominance diagrams display domains of predominance of chemical compounds (in this example, copper compounds in an atmosphere containing sulfur and oxygen) as a function of chemistry of the gas atmosphere of the system.

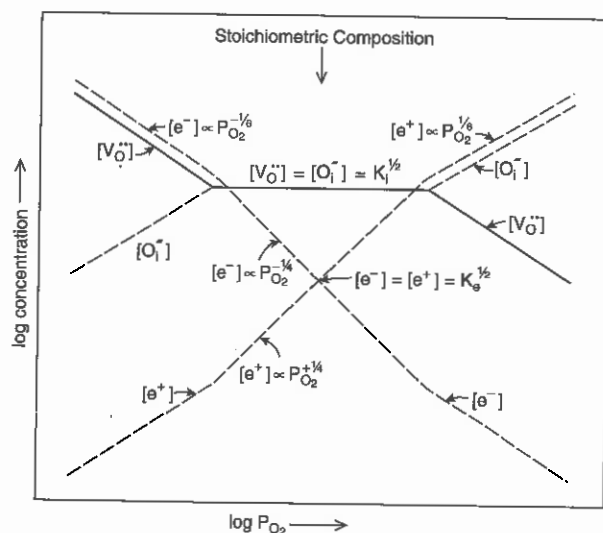


FIGURE 1.8 Sketch of the variation of the concentration of crystal defects of an oxide with departure from the stoichiometric composition of the compound, here represented by the equilibrium partial pressure of oxygen in the atmosphere, which controls such departures.

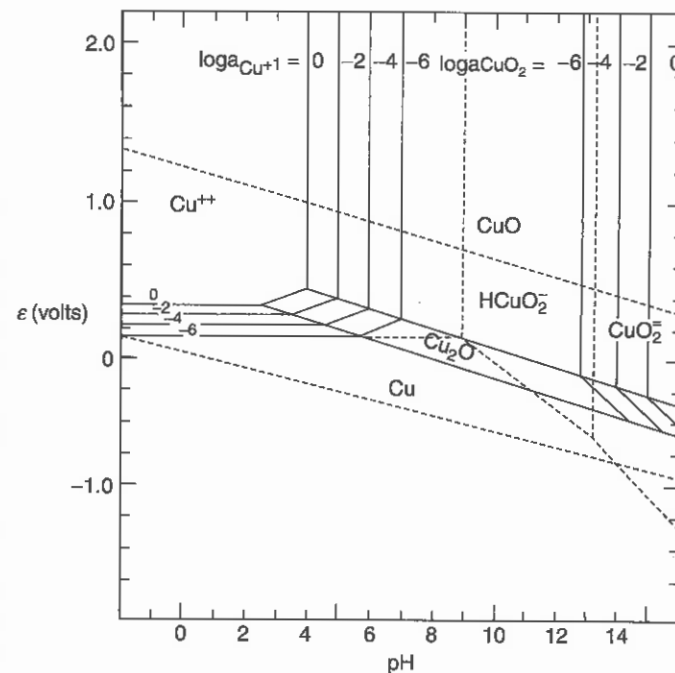


FIGURE 1.9 Pourbaix diagram displays domains of predominance of ionic and nonionic components in aqueous solutions containing copper as a function of the impressed emf and the hydrogen potential of the mixture.

traditional predominance diagrams illustrated in Figure 1.7. In this kind of application the variables subject to control to determine the surroundings are the pH of the aqueous environment and the magnitude of an electromotive force applied to the system. In the domain where Cu is predominant the metal is said to be immune to corrosion; copper corrodes in domains where ionic forms predominate in the aqueous environment. In other regions a compound predominates; it may form on the surface of the copper and protect the metal from corrosion resulting in passivation of the material.

This sampling of the kinds of maps that can be generated from thermodynamic data is by no means exhaustive. New forms can be created by choosing other variables to form the axes of the map. Additional information (e.g., iso-activity lines on a phase diagram) can be superimposed on these maps. These maps all share the attribute that they represent competition for stability or predominance among the various forms that the atoms of the elements in the system may exhibit. Each has an appropriate set of database information required to generate the map, and each has an underlying principle that determines the competition and an underlying strategy for connecting database to map. Each has its realm of applications that address appropriate versions of the question, "what happens?"

1.5 THREE LEVELS OF THE THERMODYNAMIC APPARATUS

What determines how matter behaves? There are three levels of sophistication that are used in answering this question.

1. The phenomenological description, in which matter is treated like a structureless glop that possesses a set of properties like temperature, pressure, chemical composition, heat capacity, etc. The behavior of an evolving system is described solely in terms of changes in its properties. This level of description contains no information about the underlying structure of matter that determines these properties. Relationships between properties are described, but there is no attempt to explain the source of values of these properties.
2. The statistical description, which recognizes that matter is composed of atoms that exist in different structural arrangements like gas, liquid, crystal, molecule. The individual atoms have properties (size, mass, electronegativity, energy, etc.); pairs of atoms (bonds) have properties associated with the interactions between the atoms (bond strength, bond energy). The behavior of a system is derived by statistical strategies that connect the properties of these units to the properties of the huge collection of atoms that make up a system. This level of description provides an explanation of the phenomenological properties of the system in terms of the behavior of the atoms that compose it.
3. The quantum description, which recognizes that single atoms and groups of atoms have an internal structure mostly residing in the distribution of electrons in space and in associated energy in the system. This level of description explains the behavior of atoms and ensembles of atoms, and hence that of systems, at the most fundamental level.

Phenomenological thermodynamics has been the most widely used level of description in the practical application of thermodynamics. The question, "what happens?" can be answered at the phenomenological level for very complicated, practical systems. A description of this level of detail is sufficient for many (if not most) practical applications. The more profound question, "why does this happen this way?" which seeks a level of explanation of observed phenomenon requires the statistical approach, and, even more fundamentally, the quantum mechanical approach. These fundamental descriptions rely heavily on computational materials science in which the properties of large collections of atoms are computed from sophisticated models for the interactions between atoms in the structure. Explanations provided by these first principle calculations have the potential for provoking new insights that ultimately may permit the prediction of database properties that have not yet been measured, or the extrapolation of results for simple systems to more complex ones. Because thermodynamics identifies the properties needed to predict the behavior of matter, thermodynamics is the basis for establishing the focus of these more fundamental scientific endeavors.

1.6 SUMMARY

- Thermodynamics provides the basis for answering the question, "if I take System A in Surroundings I and put it into Surroundings II, what will happen?"
- Thermodynamics is important because it is pervasive, comprehensive, established, the basis for organizing information about the behavior of physical systems and for developing maps of equilibrium states.
- Maps of equilibrium states are used to supply answers to the "what happens?" question for a wide variety of systems in a wide variety of surroundings.
- The behavior of matter has been described at three different levels of sophistication: (1) phenomenological thermodynamics, (2) statistical thermodynamics, (3) quantum statistical thermodynamics.

2 The Structure of Thermodynamics

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Figure 1.4 provides a visualization of the structure of thermodynamics. At its apex are a very few very general, and therefore very powerful, principles: the laws of thermodynamics. From these few principles can be deduced predictions about the behavior of matter in a very broad range of human experience, frequently expressed in the form of the equilibrium maps that descend from the apex. An understanding of how matter behaves in every situation rests directly upon these laws.

In their simplest and most general form the laws apply to the universe as a whole:

1. There exists a property of the universe, called its energy, which cannot change no matter what processes occur in the universe.
2. There exists a property of the universe, called its entropy, which can only change in one direction no matter what processes occur in the universe.
3. A universal absolute temperature scale exists and has a minimum value, defined to be absolute zero, and the entropy of all substances is the same at that temperature.

More precise, mathematically formulated statements of the laws are developed in Chapter 3.

In practice, the focus of thermodynamics is on a subset of the universe, called a system, (Figure 2.1). In order to apply thermodynamics, the first step is to identify the subset of the universe that encompasses the problem at hand. It is necessary to be explicit about the nature of the contents of the system, and the specific location and character of its boundary.

The condition of the system at the time of observation is described in terms of its properties, quantities that report aspects of the state of the system such as its temperature, T , its pressure, P , its volume, V , its chemical composition, and so on. As the system is caused to pass through a process its properties experience changes (Figure 2.1). A very common application of thermodynamics is a calculation of the changes that occur in the properties of some specified system as it is taken through some specified process. Thus, an important aspect of the development of thermodynamics is the deduction of relationships between the properties of a system, so that changes in some properties of interest, e.g., the entropy of the system, may be computed from information given or determined about changes in other properties of the system, e.g., temperature and pressure.

An understanding of the structure of thermodynamics is aided greatly by deliberately organizing the presentation on the basis of a series of classifications, which compartmentalize these characteristics of the field, and thus permit a focus upon the subset of the thermodynamic apparatus that is appropriate to a specific problem. Accordingly, presented in this chapter are classifications of:

1. Thermodynamic systems.
2. Thermodynamic properties.
3. Thermodynamic relationships.

Mastery of the strategy for developing relationships among the properties of thermodynamic systems paves the way for deducing the sets of working equations that are of most practical importance in thermodynamics: the conditions for equilibrium. These equations are the basis for developing the maps of equilibrium states discussed in Chapter 1. A general criterion that may be used to determine when a system has attained thermodynamic equilibrium is introduced in Section 2.4. This concept is developed precisely and mathematically in Chapter 5, along with a general strategy for finding the conditions for equilibrium in the most complex kind of thermodynamic system.

2.1 A CLASSIFICATION OF THERMODYNAMIC SYSTEMS

The complete thermodynamic apparatus is capable of evaluating the equilibrium conditions of the most complex kind of system as it experiences the full range of potential influences that have been identified that may affect its condition. Most practical problems in thermodynamics do not require the invocation of the whole thermodynamic structure for their solution. In order to pinpoint the part of the apparatus that must be used to handle a given case, it is useful to devise a classification of thermodynamics systems. Use of such a classification at the beginning of consideration of any problem serves to focus attention on the specific set of influences that may operate, and, perhaps more important, those that may be excluded from consideration. This classification also serves as a basis for laying out the sequence of presentation in this text.

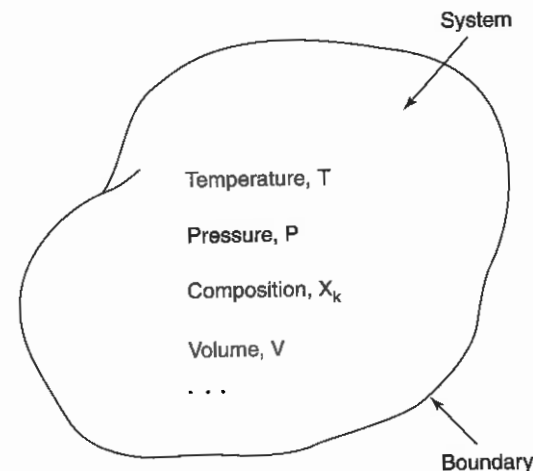


FIGURE 2.1 The subset of the universe in focus in a particular application of thermodynamics is usually called the system. At any given instant of observation the condition of the system is described by an appropriate set of properties. Limitations on changes in these properties are set by the nature of its boundary.

At the outset of consideration of any problem, classify the system under study according to each of the following five categories:

1. Unary vs. multicomponent.
2. Homogeneous vs. heterogeneous.
3. Closed vs. open.
4. Nonreacting vs. reacting.
5. Otherwise simple vs. complex.

Each of these descriptive words has explicit meaning in thermodynamics.

Category 1 identifies the complexity of the chemistry of the system. Systems with the simplest chemical composition are unary, which means: one chemical

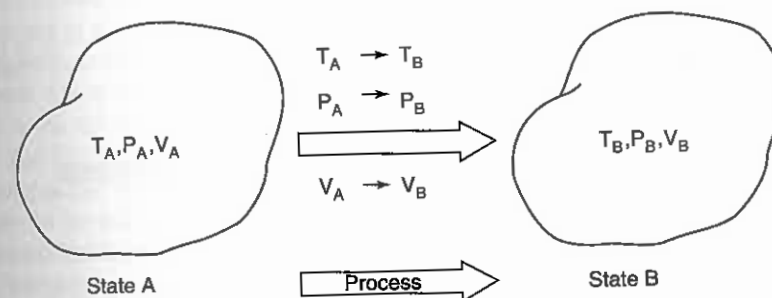


FIGURE 2.2 A process is a change in the condition or state of the system. Properties change from their values in some initial state A to some final state B.

component. If a system has more than one chemical component, i.e., is multicomponent, additional apparatus must be devised to describe its behavior; its composition may vary.

The word homogeneous in category 2 has a specific thermodynamic meaning: single phase. If a system is composed of more than one phase (e.g., a mixture of water and ice), it is heterogeneous. Treatment of heterogeneous systems adds to the thermodynamic apparatus.

In category 3, closed has a specific thermodynamic meaning: closed describes a system that makes no exchanges of matter with its surroundings for the processes being considered. If matter is transferred across the boundary, the system is an open system, and terms must be added to allow for changes in condition associated with the addition of matter to the system.

Category 4 brings into consideration systems that can exhibit chemical reactions and focuses upon the additional apparatus required to describe chemical reactions.

The last category lumps all other influences into a single listing. If a system is capable of exhibiting kinds of energy exchange other than those arising from thermal, mechanical or chemical changes, e.g., if in the problem at hand there may be involved gravitational, electrical, magnetic or surface influences, then it is classified as complex in this category. If none of these special kinds of influences operates in the problem at hand, it is an otherwise simple system.

Figure 2.3 is a cross-section through a thin film device. From the point of view of thermodynamics the system consists of a large number of chemical components, some as impurities added to control the electronic properties, distributed through several phases. Chemical reactions may occur at the gas/solid interface and between the solid phases. Thus, during processing this system may be classified as a multicomponent, multiphase, closed, reacting, otherwise simple system.

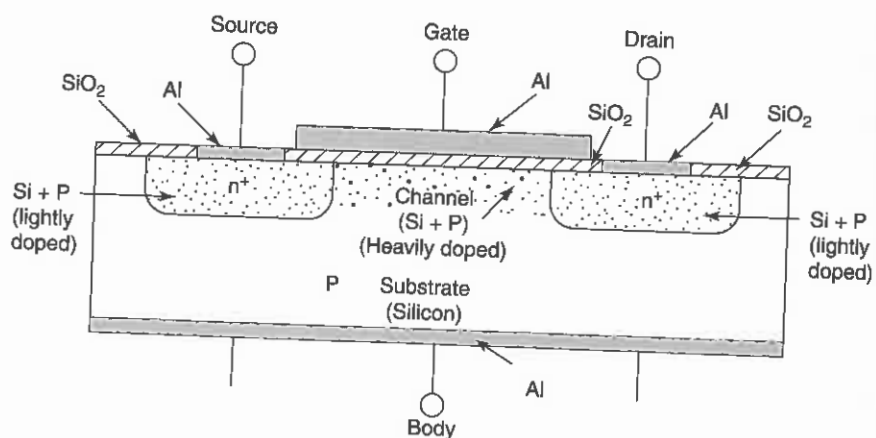


FIGURE 2.3 Cross-section through a MOSFET (metal oxide semiconductor field effect transistor) thin film device shows it to be a multicomponent, multiphase system in which chemical reactions and the influence of an electric field are important.

The most rudimentary kind of system that may be encountered is classified as an unary, homogeneous, closed, nonreacting, otherwise simple system. This classification of simplest of systems is the focus of Chapter 4. Chapter 7 introduces unary heterogeneous systems. Chapter 8 presents the apparatus for handling multicomponent, homogeneous systems. Multicomponent, heterogeneous systems are dealt with in Chapters 9 and 10. The apparatus for handling reacting systems is contained in Chapter 11. Complex systems are dealt with in Chapters 12 to 15. The text progresses through a sequence of classes of systems of increasing complexity until, at the end, the tools for describing the behavior of matter in the most complicated kind of system: multicomponent, heterogeneous, open, reacting, complex are in hand.

2.2 CLASSIFICATION OF THERMODYNAMIC VARIABLES

The internal condition of a thermodynamic system, the changes in its condition, and the exchanges in matter and energy, which it may experience, are quantified by assigning values to variables that have been defined for that purpose. These variables are the mathematical stuff of thermodynamics; their evaluation is the justification for inventing the apparatus in the first place. They fall into two major classes: state functions and process variables.

2.2.1 STATE FUNCTIONS

A state function is a property of a system that has a value that depends upon the current condition of the system and not upon how the system arrived at that condition. The temperature of the air in the room has a certain value at the moment which does not depend upon whether the room heated up to that temperature or cooled down to it. Other familiar properties that have this attribute are: pressure, volume and chemical composition. Figure 2.4 shows the mathematical nature of a state function.

One of the great accomplishments of thermodynamics is the identification of these and other properties of systems, perhaps not so familiar, which are also functions only of the current condition of the system. These include various measures of the energy of the system, its entropy, a variety of properties associated with components in solutions, and properties associated with complex aspects of the system. Complete definitions of these properties are first developed in Chapters 3 and 4; the list is expanded as the apparatus in later chapters requires.

The fact that such state functions exist gives rise to one of the most important strategies for the thermodynamic analysis of the complicated processes that are likely to be encountered in the real world of science and technology. A process converts the condition of a system from some initial state, A, to some final state, B. Precisely because this class of properties, state functions, depends only upon the state of the system, the change in any state function for any process is always simply its value for the final state minus its value for the initial state. Thus, the change in any state function must be the same for every process that converts the system from the

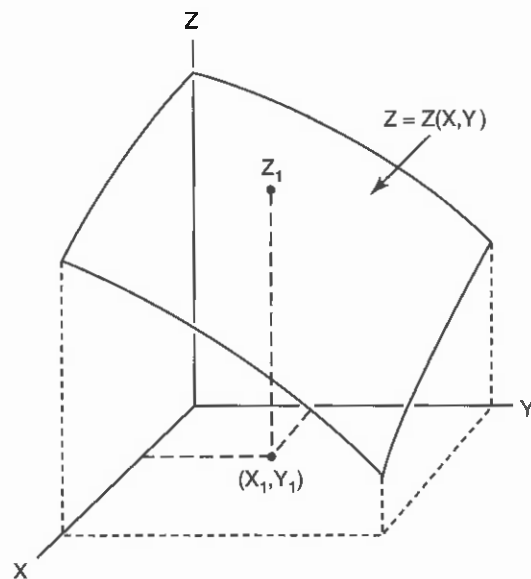


FIGURE 2.4 If the value of the variable Z depends only upon the current values of the variables X and Y , then all three variables are state functions. The functional relationship among these variables, written $Z = Z(X, Y)$, is represented by a surface in X, Y, Z space. For any given values (X_1, Y_1) there is a corresponding value $Z = Z_1$.

same initial state A to the same final state B. The value for the change in any state function is independent of the path (sequence of intermediate states) or process by which the system is converted from state A to state B (Figure 2.5). As a consequence, the change in any state function accompanying a very complicated real-world process, which alters the system from state A to state B, may be computed by concocting or imagining the simplest process that connects the same two end states. A computation of the changes in state functions for this simple process will yield the same result as would be obtained for the very complex process.

The importance of this strategy, its application, and other consequences of the existence of state functions is developed in Chapter 4.

2.2.2 PROCESS VARIABLES

In contrast to the notion of state functions, process variables are quantities that only have meaning for changing systems. Their values for a process depend explicitly upon the path, i.e., the specific sequence of states traversed, that takes the system from state A to state B. Change is inherent to the very concept of these quantities. There are two primary subcategories of process variables: work done on the system as it changes, and heat absorbed by the system.

The concept of work is developed in classical mechanics in physics. A force acts upon a body. If the point of application of the force moves, then the force does work. Let the vector \mathbf{F} denote the force, and the vector $d\mathbf{x}$ denote an increment of its

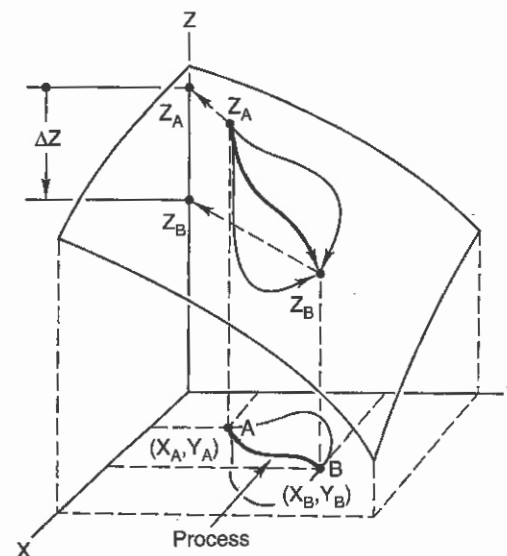


FIGURE 2.5 A process that changes the condition of the system from state A to state B may (if it is simple enough) be represented by a curve in the $(X-Y)$ plane: this represents the sequence of states through which the system passes in changing from state A to state B. Evidently, since Z is a state function, the change in Z , written $\Delta Z = Z_B - Z_A$, will be the same for all paths connecting A and B.

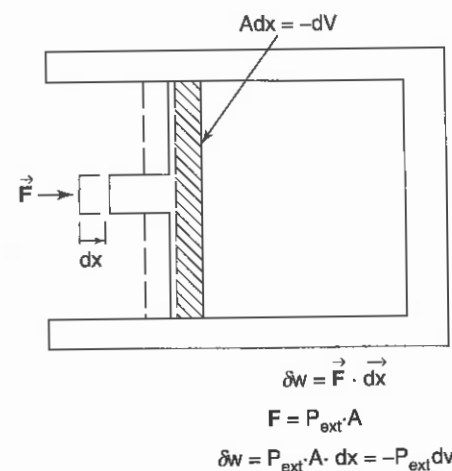


FIGURE 2.6 The generic concept of work is illustrated for mechanical work due to the external pressure acting on the system; the displacement of the force \mathbf{F} through the distance $d\mathbf{x}$ does work.

displacement (Figure 2.6). The increment of work done by this displacement is defined to be:

$$\delta w = \mathbf{F} \cdot d\mathbf{x} \quad (2.1)$$

where the notation represents the dot product of the two vectors. For a finite process the force is moved along some path through space; the value of the force and the direction of force and displacement may change as it moves. The work done is defined to be:

$$w = \int \mathbf{F}(x) \cdot d\mathbf{x} \quad (2.2)$$

where $\mathbf{F}(x)$ describes how the force varies with position, x , and the integration is a line integral along the path traversed. The mathematical details are not important in the present context. It is important to note that the displacement of the force is an inherent component in the concept of work. Work cannot be associated with a system at rest; it is a process variable.

It is possible for work to be done through a variety of influences that may act upon the system. Each of the forces that have been identified in physics:

1. The force exerted by the pressure on a system.
2. Force due to gravity.
3. Body forces in a rotating system.
4. The force acting on a charged particle in an electrical field.
5. Force on a magnetic dipole in a magnetic field.
6. The force associated with surface tension.

may be displaced to do work. The early chapters in the text limit consideration primarily to work done by the mechanical force exerted by the external pressure on the system. The remaining forces listed are in the complex system category in the classification of systems; each has its own set of thermodynamic apparatus, as developed in Chapter 12 to Chapter 15.

If the boundary of a system is rigid and impermeable so that no matter can cross it and no force acting upon it may move, the internal condition of that system can still be caused to change. There thus exists a kind of influence, which can alter the condition of a system, that is not a form of work or matter transfer. During the past three centuries concepts and methods have gradually developed that quantified this thermal influence, beginning with the development of the thermometer. A temperature scale was devised and evolved into a tool of general application. The calorimeter provided a means for determining relative quantities of this thermal energy transferred in different processes. The quantity of heat that flows into or out of a system during a process can now be determined with accuracy, at least under carefully controlled experimental conditions. Heat always carries with it a change in the condition of a system; it is thus also a process variable. Just as is true for work, it is meaningless to visualize a quantity of heat associated with a system that is not changing; the notion of the heat content of a system is meaningless. Flow and change are inherent aspects of the nature of heat.

2.2.3 EXTENSIVE AND INTENSIVE PROPERTIES

State functions may be further classified as extensive or intensive properties of the system.

If the value of the property is reported for the system as a whole, then it is called an extensive property of the system. For example, the volume V of a system is an extensive property. The number of moles of a given chemical component n_k in the system is extensive, as are the internal energy U and entropy S , to be defined in Chapter 3. In general, extensive properties depend upon the size or extent of the system. The most direct measure of size of a system is the quantity of matter that it contains. In a comparison of two systems, which have identical intensive properties, doubling the quantity of matter doubles all of the extensive properties.

A property of the system is intensive if it may be defined to have a value at a point in the system. For example, temperature T is an intensive thermodynamic property; the temperature has a value at each point in the system and may indeed vary from point to point. Pressure P may also be defined at each point in the system; in the Earth's atmosphere, pressure varies with height as well as horizontally. Maps of this variation are routinely presented in weather reports.

It is possible to derive an intensive property for each of the extensive properties defined in thermodynamics. Such a definition visualizes a limit of the ratio of two extensive properties in a small region of the system. For example, the molar concentration of a component k , c_k (moles of component k /liter), may be defined at a point by visualizing a small volume element neighboring the point (ΔV) and the number of moles of component k (Δn_k) in that element. The concentration is the limit of the ratio

$$c_k = \lim_{\Delta V \rightarrow 0} \frac{\Delta n_k}{\Delta V} \quad (2.3)$$

as ΔV approaches zero. This strategy may be used to define densities of internal energy, entropy, and any of the other extensive properties defined in Chapter 4. A rigorous development of these concepts is given in Chapter 14.

Similar definitions may be developed by reporting extensive properties per mole of matter in the system. Thus, the entropy per mole or volume per mole of the system may be defined for volume elements in the system and may vary from point to point. The most familiar and widely used example of molar properties is the mole fraction of component k , X_k (see Chapter 8), used to describe chemical composition. The mole fraction is the limit of the ratio of the number of atoms (or molecules) of component k to the total number of atoms or molecules in the volume element as the total number of moles goes to zero. This measure of composition may vary from point to point in the system.

It may be confusing to find some intensive properties treated as if they were properties of the system as a whole. For example, a value for the temperature, pressure, or the atom fraction of CO_2 in a gas mixture may be reported for the system. However, this is only possible in the special case, which is frequently encountered in introductory thermodynamics, in which these intensive properties do

not vary with position for the system under consideration. It is possible to quote a value of the temperature for a system if, and only if, the temperature is uniform in that system. Intensive properties, by concept, may be defined at each point in a system, and have the potential to vary from point to point. If in simple systems they do not happen to vary then they have a single value that describes that property for the system. However, this does not convert them into extensive properties.

By their nature, intensive properties can only depend upon the values of other intensive properties. It is clear that the value of a property, which may be defined at a point in the system, cannot depend upon the value of another property that is a characteristic of the whole system. Extensive properties may be expressed as integrals of intensive properties over the extent of the system (see Chapter 14).

2.3 CLASSIFICATION OF RELATIONSHIPS

The apparatus of thermodynamics provides connections between the properties in a system. These connections are frequently unexpected: they may not be intuitively evident. For example, how the entropy of a system varies with pressure is determined by the coefficient of thermal expansion of the system, as will be demonstrated in Chapter 4. The apparatus also provides equations for computing changes in these properties when a specified system is taken through a specified process. Also, thermodynamics introduces a variety of variables that are defined in terms of previously defined quantities. As a result, the formalism of thermodynamics generates a large number of relationships between the quantities with which it deals. The potential confusion that might result may, to some extent, be relieved by organizing the presentation of the relationships in thermodynamics.

This section introduces a classification of thermodynamic relationships so that this formidable array of equations may be subdivided into categories that reflect their origin:

1. The laws of thermodynamics are the fundamental equations that form the physical basis for all of these relations.
2. Definitions present new measures of the energy of systems expressed in terms of previously formulated variables. These defined quantities are generally introduced because they simplify the description of some particular class of system or process that may be commonly encountered. Another set of definitions introduces the quantities that are commonly measured in the laboratory and reported in thermodynamic databases.
3. Coefficient relations emerge from the description of changes in state functions during an infinitesimal step in a process. The differential relation

$$\overset{\text{extensive}}{dZ} = M \overset{\text{intensive}}{dX} + N dY + \dots \quad (2.4)$$

describes in a formal way how the state function Z (the dependent variable in this relation) changes as a result of changes in the functions (X, Y, \dots)

(the independent variables) that describe the state of the system. The coefficients in this equation are related to specific partial derivatives of Z :

$$M = \left(\frac{\partial Z}{\partial X} \right)_Y \quad \text{and} \quad N = \left(\frac{\partial Z}{\partial Y} \right)_X \dots \quad (2.5)$$

This differential equation is illustrated for two independent variables in Figure 2.7. These coefficient relations frequently establish connections between variables that are not intuitively obvious.

4. Maxwell relations also derive from the mathematical properties of state functions. In order for Equation 2.4 to be mathematically valid, it is necessary and sufficient that:

$$\left(\frac{\partial M}{\partial Y} \right)_{X, \dots} = \left(\frac{\partial N}{\partial X} \right)_{Y, \dots} \quad (2.6)$$

Since every state function may be expressed as functions of all of the possible combinations of the others (see Chapter 4), equations of the form Equation 2.5 abound in thermodynamics. Maxwell relations hold for all of these equations.

5. Conditions for equilibrium are sets of equations that describe the relationships between state functions, which must exist within a system, when it attains its equilibrium state. These are the working equations for calculating the maps of equilibrium states discussed in Chapter 1.

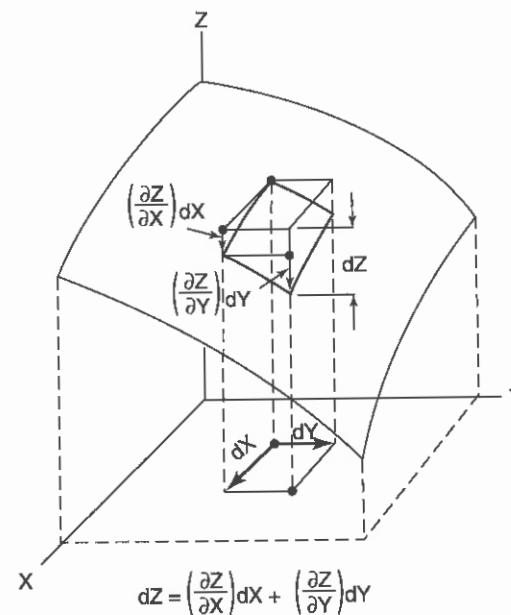


FIGURE 2.7 Geometrically, the change dZ associated with the changes dX and dY is given by the slope of the surface in the X direction times dX plus the slope of the surface in the Y direction times dY .

The laws are developed with precision and generality in Chapter 3. In Chapter 4, definitions and the mathematical basis for coefficient and Maxwell relations are presented in detail, together with examples for their application. Derivations of the conditions for equilibrium and systematic application of these equations to generate equilibrium maps for systems of increasing complexity occupy most of the remainder of the text.

2.4 CRITERION FOR EQUILIBRIUM

A system placed in a new set of surroundings will change spontaneously until it has exhausted its capacity for change. When a system attains this final state of rest it is described as being in equilibrium with itself and its surroundings. The prediction and description of this equilibrium state for any given system is a problem of central importance in thermodynamics. This description is expressed in terms of a set of equations, called the conditions for equilibrium, which are relationships among the internal properties that must obtain in order for the system to be at rest. As a simple and familiar example of such equations, consider a unary, two phase, closed, nonreacting otherwise simple system consisting of ice floating in water. The condition for thermal equilibrium in this system is evidently

$$T^{\text{ice}} = T^{\text{water}} \quad (2.7)$$

Additional conditions must apply in order for the system to be in complete equilibrium.

The conditions for equilibrium are extremely important in thermodynamics. For the most complex kind of system these equations may be deduced from a single principle: the general criterion for equilibrium. This powerful principle, which follows directly from the second law of thermodynamics, is the subject of Chapter 5. The remainder of the text deals chiefly with the repeated application of this general criterion to the deduction of equations describing the equilibrium state for each category in the hierarchy of the classification of thermodynamic systems introduced at the beginning of this chapter, and the application of the resulting equations to computing equilibrium maps and solving practical problems in thermodynamics.

2.5 SUMMARY

Thermodynamics provides the basis for describing the behavior of arbitrarily complex physical systems. This description flows from the laws of thermodynamics:

- Energy is conserved.
- Entropy is created.
- Temperature has a zero.

The part of the apparatus of thermodynamics required to handle a given problem may be brought into focus by classifying the system under consideration according to:

- Its number of components.
- Its number of phases.
- The permeability of its boundary.
- Its ability to exhibit chemical reactions.
- Its interactions with nonmechanical forces.

The strategy of presentation in this text is based upon a progressive development of systems of increasing complexity in this hierarchical classification.

Changes in the condition experienced by such a system are described in terms of state variables, with values that depend only upon the current condition of the system; and process variables, which only have meaning for processes, i.e., changes in state of the system.

Changes in state functions are independent of the process by which the system passes from its initial to its final condition. Thus, these changes may be computed by visualizing the simplest process connecting the end states, and making the calculation for that process.

Properties of thermodynamic systems are either intensive, if in concept they are defined at each point in the system or extensive, if they report an attribute of the system as a whole.

Changes in properties may be evaluated for any system taken through any process by applying the relationships of thermodynamics if an appropriate database exists for that system. Knowledgeable manipulation of this potentially bewildering array of relationships is aided by classifying them as

- The laws of thermodynamics.
- Definitions.
- Coefficient relations.
- Maxwell relations.
- Conditions for equilibrium.

A general criterion for equilibrium forms the basis for deducing these conditions for equilibrium. The conditions for equilibrium lead directly to the working equations that yield maps of equilibrium states for that system. The maps in turn permit the prediction of the behavior of matter in the most complex kinds of systems.

HOMEWORK PROBLEMS

Problem 2.1. Classify the following thermodynamic systems in the five categories defined in Section 2.1:

- a. A solid bar of copper.
- b. A glass of ice water.

- c. A yttrium stabilized zirconia furnace tube.
- d. A Styrofoam coffee cup.
- e. A eutectic alloy turbine blade rotating at 20,000 r/min.

You may find it necessary to qualify your answer by defining the system more precisely; state your assumptions.

Problem 2.2. It is not an overstatement to say that without state functions thermodynamics would be useless. Discuss this assertion.

Problem 2.3. Determine which of the following properties of a thermodynamic system are extensive properties and which are intensive:

- a. The mass density.
- b. The molar density.
- c. The number of gram atoms of aluminum in a chunk of alumina.
- d. The potential energy of a system in a gravitational field.
- e. The molar concentration of NaCl in a salt solution.
- f. The heat absorbed by the gas in a cylinder when it is compressed.

Problem 2.4. Why is heat a process variable?

Problem 2.5. Write the total differential of the function:

$$z = 12u^3v\cos(x)$$

- a. Identify the coefficients of the three differentials in this expression as appropriate partial derivatives.
- b. Show that three Maxwell relations hold among these coefficients.

Problem 2.6. Describe what the notion of equilibrium means to you. List as many attributes as you can think of that would be exhibited by a system that has come to equilibrium. Why do you think these characteristics of a system in equilibrium are important in thermodynamics?

3 The Laws of Thermodynamics

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The laws of thermodynamics, at the apex of Figure 1.4, are highly condensed expressions of a broad body of experimental evidence. The formulation of these succinct empirical statements about the behavior of matter was essentially completed by the end of the 19th century and has not required significant alteration in the light of scientific experience since that time. This is a remarkable fact in view of the enormous scientific progress that has been achieved in the 20th century. The laws of thermodynamics are thus soundly based and broad in their application.

The laws are empirical: derived from experimental observations of how matter behaves. No claim is made that they may be deduced from any fundamental philosophical principles.

The laws of thermodynamics have a status in science that is similar to Newton's laws of motion in mechanics and are similarly subject to potential revision in the light of new information. When it was found in physics that new evidence could only be explained by modifying Newton's laws with Einstein's relativistic concepts, the laws of motion were generalized. However, this generalization was in such a form that the new equations simplify to Newton's laws when the velocity of the system is not a significant fraction of the velocity of light. Newton's laws were not abandoned; they were expanded to include newly discovered phenomena. Classical mechanics could be viewed as a special case of the new relativistic mechanics. This strategy was necessary because classical mechanics successfully described a great body of scientific observations with plausibility and precision.

It is possible that new experimental evidence could require a reformulation of the laws of thermodynamics. Up to now this has not been necessary, although the discovery of nuclear energy has had to be accommodated by expanding the framework established in the 19th century.

4 Thermodynamic Variables and Relations

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System A in Surroundings I is placed in Surroundings II. What will happen?

This chapter supplies answers to that question for the simplest class of thermodynamic system: a unary, homogeneous, closed, nonreacting, otherwise simple system. A part of the answer to the question, "What will happen?" is the more specific question, "What changes will occur in its properties?" Strategies for computing thermodynamic properties, referred to in Figure 1.4, begin with methods developed for such simple systems.

So far we have defined the following variables:

Process variables (values depend on the path specified for the process):

Q — heat absorbed (joules).

W — mechanical work done on the system (joules).

W' — all other kinds of work done on the system (joules) (equal to 0 for the simplest systems in this chapter).

State variables (values depend only upon the current state):

T — temperature (K).

P — pressure (atmospheres).

U — internal energy (joules).

S — entropy (joules/K).

V — volume (cubic meters).

Additional state variables will be defined in terms of these variables in this chapter.

It is established that, in such a simple system in equilibrium with itself and its surroundings, the state is completely specified by two variables.¹ For example, if the temperature and pressure are specified then the state of such a system is fixed. This statement implies that the values of all other state properties (so far, V , U and S) of this system are determined given values of the variables (T , P). Functions exist connecting these properties to T and P : e.g., $V(T, P)$ implies that for each value of (T , P) for a given substance there is a corresponding value of its molar volume. This relationship may be represented graphically as a surface over the (T , P) plane. Each substance has its own surface $V(T, P)$ describing how its molar volume varies with temperature and pressure. For example, the molar volume (volume per mole) of liquid water is a different function of T and P than that for water vapor. At ordinary temperatures and pressures 1 mol of water vapor is about 20,000 times larger than 1 mol of liquid water. The molar volume of lead is roughly twice that of aluminum.

Since U and S are also state functions it follows that for any given substance they also have functional relations to T and P . Thus, for example, for solid copper there exist surfaces over the (T , P) plane for $U(T, P)$ and $S(T, P)$. The additional state functions defined in this chapter each have their own functional relationships to T and P , and their own surfaces over the (T , P) plane.

This chapter also introduces a set of experimental variables: properties of materials that are measured in laboratories, assessed, and gathered into databases for application in thermodynamic calculations. These properties are familiar from introductory chemistry and physics courses:

α — the volume coefficient of thermal expansion (with units K^{-1}).

β — the volume coefficient of compressibility (with units atm^{-1}).

C_P — the heat capacity at constant pressure (with units J/K).

C_V — the heat capacity at constant volume (with units J/K).

These properties are also functions of temperature and pressure for each substance. This chapter introduces procedures for computing all of the state functions for a simple system from these database properties.

Since all of the state functions that will be defined are related to temperature and pressure, it may be concluded that they are all related to each other. These relationships may also be derived from database information.

¹ To evaluate extensive properties of the system one needs in addition the total number of moles n_T of components contained in the system. A common strategy evaluates extensive properties per mole of system. Results per mole are easily converted to values for the system by multiplying by n_T .

The simplest class of problems that may be solved thermodynamically is those in which some change in the condition or properties of a system is brought about by controlled or measured changes in the influences that may operate on the system. A few representative examples are:

- Hydrogen gas in a 20-l steel cylinder at ambient temperature (18°C) is found to be at 10 atmospheres of pressure. Is the pressure significantly affected if the room temperature heats up to 25°C ?
- Calculate the change in entropy of 50 g of nickel when it is heated from 0 to 500°C at one atmosphere pressure.
- A 40-g sample of the elastomer, polyisoprene, is stretched so that its length increases by 50%. Estimate the change in temperature of the sample if it is initially at 20°C .
- Estimate the amount of heat required to raise the temperature of an alumina (Al_2O_3) charge weighing 50 kg from room temperature to 1350°C at one atmosphere pressure.

Solutions to these problems are based upon relationships between the properties given and required; the strategy for deriving such relationships is the subject of this chapter.

The first step in applying this strategy is the translation of the problem encountered in the real-world (or in the text) from English into thermodynamics. This exercise in translation has the following elements:

- Identify the properties of the system about which information is given. For example, in problem b these properties are:

Temperature (T) (changes from 0 to 500°C).

Pressure (P) (remains fixed at one atmosphere).

These variables are called the *independent variables* in the problem because they are subject to experimental control in the context of the problem and thus may be changed independently.

In simple systems there are two independent variables.

- Identify the property in the system about which you are seeking information. In problem b, this property is the entropy of the system. This property is called the *dependent variable* in the problem because its value is determined by the changes in the controlled (independent) variables.

- Find or derive a relationship between the sought (dependent) variable and the given (independent) variables. In problem b, this relation has the generic form: $S = S(T, P)$, read "entropy as a function of temperature and pressure."

This relationship will necessarily contain quantities that are properties of the material that makes up the system, such as heat capacity, thermal expansion coefficient, and the like.

4. Obtain values for these quantities, either from tabulations such as those reviewed in Appendices B and E, from the literature, compiled databases or, if necessary, by direct experimental evaluation.
5. Substitute these values into the relationship and carry out the mathematical operations necessary to obtain a numerical value for the dependent variable in the problem.

This strategy will be applied repeatedly in this and subsequent chapters to yield numerical answers to practical problems.

The crucial application of the principles of thermodynamics in this strategy is evidently contained in step 3, which requires the derivation or deduction of the relationship that connects the dependent variable in the problem to the independent variable through database information. A general procedure for deriving such relationships is the focus of this chapter.

4.1 CLASSIFICATION OF THERMODYNAMIC RELATIONSHIPS

Thermodynamics abounds with relationships. This potentially confusing aspect of the structure of thermodynamics exists because a variety of state functions are defined in terms of other state functions. This potentially bewildering array of equations may be tamed by organizing them into five classifications introduced in Section 2.3 in Chapter 2:

- I. The laws of thermodynamics.
- II. Definitions in thermodynamics.
- III. Coefficient relations.
- IV. Maxwell relations.
- V. Conditions for equilibrium.

The first two categories are self-explanatory; categories III and IV are derived from mathematical properties of state functions. Relationships in category V are derived from the general criterion for equilibrium developed in Chapter 5; much of the remainder of the text focuses upon these relationships.

4.1.1 THE LAWS OF THERMODYNAMICS

The relationships in this category have been presented in Chapter 3. Succinctly reviewed, they are:

The first law:

$$dU = \delta Q + \delta W + \delta W' \quad (4.1)$$

Reversible mechanical work:

$$\delta W_{\text{rev}} = -P dV \quad (4.2)$$

Reversible heat absorbed:

$$\delta Q_{\text{rev}} = T dS \quad (4.3)$$

Combined statement:

$$dU = T dS - P dV + \delta W' \quad (4.4)$$

Equation 4.4 is a centerpiece in the mathematical framework of thermodynamics and will be applied repeatedly in subsequent developments.

4.1.2 DEFINITIONS IN THERMODYNAMICS

Relationships presented in this section are purely and simply *definitions*. There are two subcategories in this classification: the *energy functions* and the *experimental (database) variables*.

The *energy functions* are measures of the energy of a system that differ from the internal energy U originally introduced in the first law. It will be demonstrated that use of these functions simplifies the description of systems that may be subjected to certain classes of processes; they are simply more convenient measures of energy in such applications than is the function, U .

4.1.2.1 Enthalpy, H

$$H = U + PV \quad (4.5)$$

a state function, since it is defined in terms of other state functions (U , P , V). Consider a small change in the state of any system; the change in enthalpy is obtained in general by taking the differential of its definition:

$$dH = dU + P dV + V dP$$

Use the combined statement of the first and second laws, Equation 4.4, to substitute for dU in this equation:

$$dH = [T dS - P dV + \delta W'] + P dV + V dP$$

Simplify:

$$dH = T dS + V dP + \delta W' \quad (4.6)$$

This equation is an alternate form of the combined statement of the first and second laws of thermodynamics. It has the same level of generality and pervasiveness as Equation 4.4.

Historically, the enthalpy function was introduced because it was convenient in the description of heat engines taken through cycles. Only mechanical work is done

in this case ($\delta W' = 0$) and cycles occur at atmospheric pressure ($dP = 0$). Thus, for such *isobaric* processes in simple systems,

$$dH_P = T dS_P = \delta Q_{\text{rev},P}$$

For this class of process (and *only* for this class) the state function defined as the enthalpy provides a direct measure of the reversible heat exchanges of the engine with its surroundings. For this reason, the enthalpy is sometimes called the *heat content* of the system. This notion is potentially very misleading. A system at rest does not contain a "quantity of heat"; heat is a process variable and only has a value for a system that is changing its state. The *change* in the state function H is related to the process variable, Q , but only for reversible, isobaric processes.

4.1.2.2 Helmholtz Free Energy, F

$$F \equiv U - TS \quad (4.7)$$

is also a state function. Again consider a small arbitrary change in the state of any system. The change in Helmholtz free energy is

$$dF = dU - T dS - S dT$$

Substitute for dU from Equation 4.4:

$$dF = [T dS - P dV + \delta W'] - T dS - S dT$$

Simplify:

$$dF = -S dT - P dV + \delta W' \quad (4.8)$$

This is yet another alternate form of the combined statement of the first and second laws which may be used to relate property changes in any system taken through any process. This function was devised because it simplifies the description of systems subject to temperature control, which is a common experimental scenario in the laboratory. If the process is carried out at constant temperature (*isothermally*) then $dT = 0$ at each step along the way. For isothermal processes,

$$dF_T = -P dV_T + \delta W'_T = \delta W_T + \delta W'_{T,T} = \delta W_{T,\text{tot}}$$

That is, for isothermal processes, the Helmholtz free energy function reports the *total (reversible) work done on the system*. For this reason this property is sometimes called the *work function*. Indeed, in Helmholtz's original presentation, he used the symbol A for this function to stand for *arbeiten*, the German word for work. This expression, i.e., the work function, may be misleading in the same way as the term heat content is misleading for the enthalpy function. A system at rest does not contain a given "quantity of work"; work can only be associated with a change in

state along a specified path. The *change* in the state function F is related to the total work done on the system only for isothermal, reversible processes.

4.1.2.3 Gibbs Free Energy, G

$$G \equiv U + PV - TS = H - TS \quad (4.9)$$

is evidently also a state function since it is also defined in terms of other state functions. Following the strategy used for the other two functions, for an arbitrary infinitesimal change in state, the change in Gibbs free energy is

$$dG = dU + P dV + V dP - T dS - S dT$$

Again substitute Equation 4.4:

$$dG = [T dS - P dV + \delta W'] + P dV + V dP - T dS - S dT$$

Simplify:

$$dG = -S dT + V dP + \delta W' \quad (4.10)$$

which is yet another equivalent but alternate statement of the combined first and second laws. The Gibbs free energy function was introduced because it simplifies the description of systems that are controlled in the laboratory so that *both* temperature and pressure remain constant. For processes carried out under these conditions [*isothermal* ($dT = 0$) and *isobaric* ($dP = 0$)]

$$dG_{T,P} = \delta W'_{T,P}$$

Thus, for such processes, which include, for example, phase transformations and chemical reactions, this function reports the total work done on the system *other than mechanical work*.

Four combined statements of the first and second laws have been presented, Equation 4.4, Equation 4.6, Equation 4.8, and Equation 4.10. All represent valid ways of describing the thermodynamic changes for any system taken through any process. Each of the defined energy functions provides a simple measure of some aspect of some process variable for specifically defined classes of processes. All of these equations will be used frequently in subsequent developments. Mnemonic devices have been concocted to aid in memorizing these equations. However, it is recommended rather that the *definitions* of H , F and G be committed to memory; then the simple two-line strategy presented here derives these combined statements of the first and second laws.

A set of *experimental variables* provides the core of practical information about a specific material essential to solving thermodynamic problems involving that material. These quantities are commonly measured in the laboratory and published in extensive tables or databases, such as those contained in the Appendices B and E and in Refs. [2–7] at the end of this chapter. A significant amount of this information

is available online without charge as noted in the references. Development of this kind of information is expensive, and assessed databases for specific classes of materials (e.g., nickel-based alloys for aerospace applications) are available for purchase from companies that compile and assess the data.

The definitions of these experimental variables directly reflect the measurements involved.

The *coefficient of thermal expansion*, α , is obtained from a measurement of the volume change of the material when its temperature is increased, with the system constrained to a constant pressure. The definition:

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \text{ (K}^{-1}\text{)} \tag{4.11}$$

reports the fractional change in molar volume of a substance with temperature. The coefficient of expansion of any material substance varies with temperature, pressure, and composition of the system. Typical values of α are listed in Table 4.1 and Appendix B.

The *coefficient of compressibility*, β , is determined by measuring the volume change of the substance as the pressure applied to it is increased while the temperature is held constant. Its definition,

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \text{ (atm)}^{-1} \tag{4.12}$$

is normalized to report the fractional change in volume with increasing pressure. The derivative in this definition is inherently negative (as P is increased, V decreases); thus, inclusion of the minus sign guarantees that tabulated values of β will be positive numbers. Note that β also varies with the temperature and pressure at which it is measured and is different for different materials. Table 4.2 and Appendix B list typical values for β .

Experimental information about the thermal behavior of substances is contained in the concept of *heat capacity*. This quantity is determined experimentally by precisely measuring the rise in temperature when a small measured quantity of heat is caused to flow reversibly into the system. Since heat is a process variable, it is necessary to specify the process path that was used in a particular heat capacity measurement. Virtually all heat capacity data are measured and compiled for either of two simple processes.

If the temperature rise, dT , is measured in a system that is set up so that the pressure is held constant and the heat, δQ , is transferred reversibly, then the heat capacity at constant pressure, C_P , is obtained from the definition

$$\delta Q_{\text{rev},P} \equiv C_P dT_P \tag{4.13}$$

Measured heat capacities are normalized to obtain the value per mole of substance; thus the units of C_P in databases are (J/mol K). This experimental variable also changes with temperature, pressure, and composition. Almost all heat capacity

TABLE 4.1
Typical Values of Coefficients of Thermal Expansion α for Common Materials^a

Material	$\alpha_L \times 10^6 \text{ K}^{-1}$	$\alpha \times 10^6 \text{ K}^{-1}$
Aluminum	23.5	70.5
Chromium	6.5	19.5
Copper	17.0	51.0
Lead	29.0	87.0
Potassium	83.0	250
Sodium	71.0	213
Alumina (Al ₂ O ₃)	7.6	23
Silica (SiO ₂)	22.2	66
Silicon Carbide (SiC)	4.6	14

^a Reported values are for linear expansion coefficients, α_L ; for isotropic systems the volume coefficient $\alpha = 3\alpha_L$.

Source: Brandes, E.A., Ed., *Smithells Metals Reference Book*, 6th ed., Butterworths, London, 1983.

TABLE 4.2
Typical Values of Coefficients of Compressibility May Be Estimated from DataBase Value for the Modulus of Elasticity, E ^a

Material	$\beta \text{ (atm)}^{-1} \times 10^7$
Aluminum	12
Carbon (Graphite)	340
Copper	6.6
Iron	5.9
Tungsten	2.9
Alumina (Al ₂ O ₃)	8.3
Boron Nitride (BN)	37
Silicon Carbide (SiC)	6.5
Silica Glass	42

^a For isotropic materials $\beta = 3/E$ with properly converted units.

Sources: Reynolds, C.L., Jr., Faugham, K.A., and Baker, R.E., *Metals, J. Chem. Phys.*, Vol. 59, p. 2934, 1973; Kingery, W.D., Bowman, H.K., and Uhlman, D.R., *Ceramics, Introduction to Ceramics*, John Wiley & Sons, New York, p. 777, 1976.

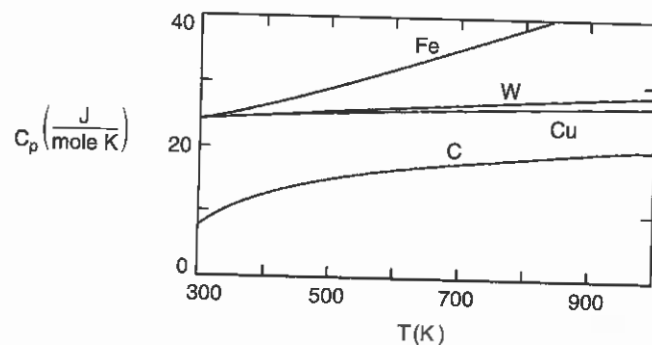


FIGURE 4.1 Variation of heat capacity with temperature for a variety of common materials.

measurements are made at one atmosphere; the pressure dependence of this quantity may be computed theoretically and can be shown to be small; the dependence upon pressure has not been widely investigated.

Figure 4.1 illustrates the temperature dependence of C_P values for a variety of substances at one atmosphere pressure and above room temperature. The variation in the temperature range below room temperature is significantly more complicated. Above room temperature, where most practical applications of thermodynamics arise, it is found that the temperature variation of C_P follows a relatively simple empirical relation:

$$C_P(T) = a + bT + \frac{c}{T^2} + dT^2 \quad (4.14)$$

Tables of heat capacity data, such as Table 4.3 and Appendix B, provide values of a , b and c for a variety of elements and chemical compounds. For precise thermodynamic computations some databases apply equations that have up to nine terms.

Heat capacity may also be measured in a system contained in a rigid enclosure so that, as the heat flows into the system, the volume of the system is constrained to remain constant. Precise measurement of the temperature rise accompanying the influx of a known quantity of heat gives the *heat capacity at constant volume*, defined in the relation

$$\delta Q_{\text{rev},V} \equiv C_V dT_V \quad (4.15)$$

After normalization, the units for C_V are also (J/mol K); C_V also varies with temperature, pressure, and composition.

For the system at constant pressure, absorption of heat results in both a temperature rise and an expansion of the volume of the system; in the case of the system constrained to constant volume, all of the heat acts to raise the temperature. Thus, more heat is required to raise the temperature of a substance one degree at constant pressure than at constant volume. It is concluded that, in general, $C_P > C_V$, and this is generally observed. It will be demonstrated in a later section that these

TABLE 4.3
Experimental Values of the Variation of Heat Capacity at Constant Pressure (C_P) for Common Materials above Room Temperature^a

Material	a	$b \times 10^3$	$c \times 10^{-5}$
Aluminum	20.7	12.3	—
Carbon (Diamond)	9.12	13.2	—
Copper	22.6	5.6	—
Gold	23.7	5.19	—
Iron (α)	37.12	6.17	—
Nickel	17.0	29.5	—
Silver	21.3	8.5	1.5
Silicon	23.9	2.5	-4.1
Tungsten	24.0	3.2	—
Alumina (Al_2O_3)	21.9	3.7	—
Silica (SiO_2)	15.6	11.4	—

^a Empirical expression for the heat capacity for this table is

$$C_P(T) = a + bT + \frac{c}{T^2}$$

Values are reported in Joules per mole.

Source: Brandes, E.A., Ed., *Smithells Metals Reference Book*, 6th ed., Butterworths, London, 1983. (Compare to Appendix D.)

two experimental variables are related to each other (see Equation 4.48); given information about α and β for the system, if one heat capacity is known the other may be computed.

It will be further demonstrated later in this chapter that if α , β and C_P are known for any simple system, i.e., one for which $\delta W' = 0$, then changes in *all* of the state functions may be computed for any arbitrary process through which that system may be taken. No additional information is required. Thus, these experimental variables are at the center of the strategy for solving practical problems that require thermodynamics. The ranges of values that these quantities may have in solids, liquids, and gases are summarized in Tables 4.1 to 4.3.

4.1.3 COEFFICIENT RELATIONS

Coefficient relations derive from the mathematical properties of functions of several variables. Since the state variables of thermodynamics have been shown to satisfy the properties of ordinary mathematical functions, these coefficient relations apply to equations among all of the state variables that have been identified and defined.

Suppose that X , Y and Z are state variables, and that there exists a relationship among these variables such that, given values for two of them, say X and Y , the third,

Z , may be evaluated. Consequences of this kind of normal mathematical functional relationship, introduced in Chapter 2 Section 2.3, are reviewed here. Mathematical shorthand for this relation is

$$Z = Z(X, Y) \quad (4.16)$$

read “ Z is a function of X and Y .” In this statement of the relationship, X and Y are “independent variables” and Z is the “dependent variable” with a value that depends upon the values that may be independently assigned to X and Y . Figure 4.2 illustrates such a relation.

Assume that this function is well behaved, i.e., is smooth and continuous with continuous derivatives. An infinitesimal step in a process may be represented by independent changes in X and Y . Owing to the functional relation, Equation 4.16, the corresponding change in Z may be written:

$$dZ = M dX + N dY \quad (4.17)$$

where the operator “ d ” implies the familiar notion of a differential of a function in elementary calculus. The coefficients in this equation are certain explicit partial derivatives:

$$M = \left(\frac{\partial Z}{\partial X} \right)_Y \quad \text{and} \quad N = \left(\frac{\partial Z}{\partial Y} \right)_X \quad (4.18)$$

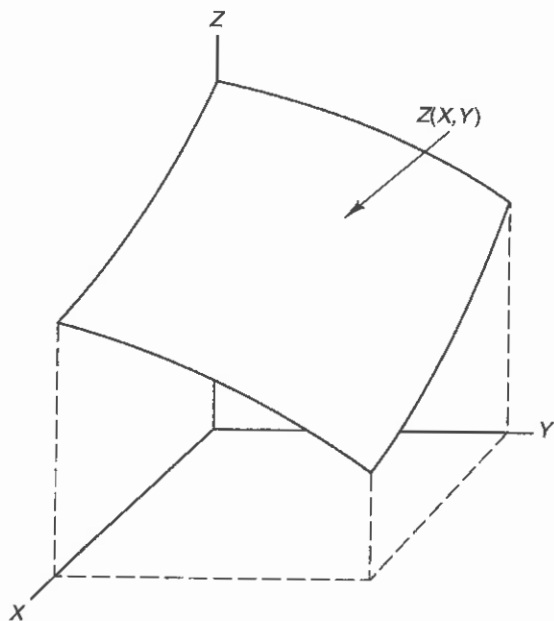


FIGURE 4.2 Geometric representation of the notion “ Z is a function of X and Y .”

The graphical meaning of these relations is evident in Figure 4.2. This equation is the formal basis for all coefficient relations. Given any thermodynamic relation among differentials of state functions it is possible, by inspection, to write down the coefficient relations. For example, the combined statement of the first and second laws, Equation 4.4, applied to processes for which $\delta W' = 0$, becomes

$$dU = T dS - P dV \quad (4.19)$$

which has the general form of Equation 4.17. The coefficients in this equation are evidently the partial derivatives:

$$T = \left(\frac{\partial U}{\partial S} \right)_V \quad \text{and} \quad -P = \left(\frac{\partial U}{\partial V} \right)_S \quad (4.20)$$

Application of this strategy to the other three combined statements derived from the definitions of the energy functions, Equation 4.6, Equation 4.8, and Equation 4.10, yields

$$T = \left(\frac{\partial H}{\partial S} \right)_P \quad \text{and} \quad V = \left(\frac{\partial H}{\partial P} \right)_S \quad (4.21)$$

$$-S = \left(\frac{\partial F}{\partial T} \right)_V \quad \text{and} \quad -P = \left(\frac{\partial F}{\partial V} \right)_T \quad (4.22)$$

$$-S = \left(\frac{\partial G}{\partial T} \right)_P \quad \text{and} \quad V = \left(\frac{\partial G}{\partial P} \right)_T \quad (4.23)$$

Since the letters in these relations represent thermodynamic quantities, these relations have physical substance.

In thermodynamic applications of this class of relations it is important to specify explicitly not only the variable in the numerator and denominator of each partial derivative but also *the variable that is being held constant*, indicated in the subscript outside the parentheses of the partial derivative. The two derivatives

$$\left(\frac{\partial H}{\partial T} \right)_P \quad \text{and} \quad \left(\frac{\partial H}{\partial T} \right)_V$$

are not equal to each other. Indeed, it can be shown that

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

It is clearly absolutely essential to be explicit about all three variables required in the specification of a partial derivative in thermodynamics.

If the state of the system is a function of more than two variables [$Z = Z(X, Y, U, V, \dots)$] the differential generalizes to

$$dZ = M dX + N dY + P dU + R dV + \dots \quad (4.24)$$

with each coefficient corresponding to a partial derivative of Z . This straightforward generalization will be useful in later chapters where more complex systems are the subject of study.

4.1.4 MAXWELL RELATIONS

This category of thermodynamic relationships also derives from the mathematical properties of state functions. Consider again variables obeying the functional relationship in Equation 4.16 with differential given by Equation 4.17. Consider again the two partial derivatives

$$M = \left(\frac{\partial Z}{\partial X} \right)_Y \quad \text{and} \quad N = \left(\frac{\partial Z}{\partial Y} \right)_X$$

Consider the following derivatives:

$$\left(\frac{\partial M}{\partial Y} \right)_X = \left[\frac{\partial}{\partial Y} \left(\frac{\partial Z}{\partial X} \right)_Y \right]_X \quad \text{and} \quad \left(\frac{\partial N}{\partial X} \right)_Y = \left[\frac{\partial}{\partial X} \left(\frac{\partial Z}{\partial Y} \right)_X \right]_Y$$

Substitute the coefficient relations for M and N given in Equations 4.18. Note that these two quantities are equal except for the order of differentiation. Thus

$$\left(\frac{\partial M}{\partial Y} \right)_X = \left(\frac{\partial N}{\partial X} \right)_Y \quad (4.25)$$

forms the mathematical basis for the Maxwell relations in thermodynamics.

In multivariable calculus, relations similar to this are called the Cauchy-Riemann conditions. They are the basis for determining whether a given differential form, e.g., $M dX + N dY$, is in fact an exact differential, i.e., whether there exists a function $Z(X, Y)$ of which $(M dX + N dY)$ is the differential. Evidently this will be so if and only if Equation 4.25 is satisfied. In thermodynamics, the establishment that Z , X , and Y are state functions guarantees that the form $(M dX + N dY)$ is always an exact differential and thus the Maxwell relations apply.

Maxwell relations for any thermodynamic differential form may be written by inspection. As examples, application of Equation 4.25 to the combined statements derived earlier yield:

$$\text{From } dU = T dS - PdV,$$

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

$$\text{From } dH = T dS + V dP,$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

$$\text{From } dF = -S dT - P dV,$$

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

$$\text{From } dG = -S dT + V dP,$$

$$-\left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P \quad (4.26)$$

These relations apply to any system at any condition. These are examples of Maxwell relations, not an exhaustive list. Equations of this form hold for every functional relationship that can be constructed joining any dependent state function to two independent ones.

To illustrate the somewhat unexpected connections between properties, which result from these relations, consider the last in the list, labeled Equation 4.26. From the definition of the coefficient of thermal expansion, Equation 4.11, it follows that:

$$\left(\frac{\partial V}{\partial T} \right)_P = V\alpha$$

Thus, from the last of the Maxwell relations, Equation 4.26,

$$\left(\frac{\partial S}{\partial P} \right)_T = -V\alpha \quad (4.27)$$

This result demonstrates that the pressure dependence of the entropy of a system is determined by its coefficient of thermal expansion, a result that is by no means intuitively evident.

The Maxwell relations are also readily generalized to systems that require more than two independent variables. Recall Equation 4.24:

$$dZ = M dX + N dY + P dU + R dV + \dots \quad (4.24)$$

Maxwell relations must hold for each pair of terms in this equation, since each

coefficient represents a differential of the state function, Z . Thus, for example,

$$\left(\frac{\partial R}{\partial X}\right)_{Y,U,V,\dots} = \left(\frac{\partial M}{\partial V}\right)_{X,Y,U,\dots}; \quad \left(\frac{\partial R}{\partial Y}\right)_{X,U,V,\dots} = \left(\frac{\partial N}{\partial V}\right)_{X,Y,U,\dots}; \quad \text{etc.} \quad (4.28)$$

EXAMPLE 4.1

It will be shown in Section 4.2 that the form of the equation relating entropy to temperature and pressure is

$$S = S(T, P) \quad dS = \frac{C_p}{T} dT - V\alpha dP$$

Write the coefficient and Maxwell relations for this equation. The coefficients of dT and dP are, respectively,

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} \quad \left(\frac{\partial S}{\partial P}\right)_T = -V\alpha$$

The Maxwell relation is

$$\left(\frac{\partial \left(\frac{C_p}{T}\right)}{\partial P}\right)_T = \left(\frac{\partial(-V\alpha)}{\partial T}\right)_P$$

Evidently how the heat capacity varies with pressure is related to the coefficient of thermal expansion for a system.

Two other relationships among partial derivatives that may be defined between the variables X , Y , and Z may be derived with the aid of results presented in this section. The *reciprocal relation*:

$$\left(\frac{\partial Z}{\partial X}\right)_Y = \frac{1}{\left(\frac{\partial X}{\partial Z}\right)_Y} \quad (4.29)$$

and the *ratio relation* (see Problem 4.2):

$$\left(\frac{\partial Z}{\partial X}\right)_Y \left(\frac{\partial Y}{\partial Z}\right)_X \left(\frac{\partial X}{\partial Y}\right)_Z = -1 \quad (4.30)$$

These equations are useful in manipulating partial derivatives in the process of developing relations between thermodynamic state functions.

As a further step in the development of the structure of thermodynamics, four classes of relationships between state functions have been presented. The laws of thermodynamics provide the physical basis for all of these relations. Definitions introduce energy functions that are convenient in specific applications and a set of

experimental variables that form the core of information needed to solve practical problems. Coefficient and Maxwell relations are consequences of the mathematical properties of differentials of state functions.

The basis for deriving the fifth category of relations, conditions for equilibrium, is presented in Chapter 5.

4.2 GENERAL STRATEGY FOR DERIVING THERMODYNAMIC RELATIONS

The relationships presented and classified in the previous section provide the basis for developing completely general equations between arbitrarily selected thermodynamic state functions. Specifically, for a system which does not do nonmechanical work, i.e., for any system for which $\delta W' = 0$, it is possible to develop an equation relating any function of the state of that system (as a dependent variable) to any pair of other state functions (as independent variables). As was pointed out at the beginning of this chapter, this is the key link in the chain of reasoning needed to translate and solve practical problems that require thermodynamics.

This section presents a general procedure for deriving such relations. The procedure is simple, straightforward, and mathematically rigorous. Since there is no mathematical sleight-of-hand involved, and because the sequence of steps to be followed is clearly defined, it should become possible to solve the most general problem with rigor and confidence.

Extension of this procedure to systems which are more general, for which $\delta W'$ is not zero, is straightforward. Applications to this kind of system, which require the development of more of the apparatus of thermodynamics, are presented in later chapters.

An exhaustive list of the state functions so far defined is given in Table 4.4; others will be introduced as more complex classes of systems are encountered and the thermodynamic apparatus expands.

TABLE 4.4
State Functions Defined in Thermodynamics

Equation of State Variables	T
Temperature	P
Pressure	V
Volume	
Energy Functions	U
Internal Energy	H
Enthalpy	F
Helmholtz Free Energy	G
Gibbs Free Energy	S
Entropy	

The general procedure begins by choosing temperature and pressure as independent variables, since these are most frequently encountered in practical problems, and deriving relations for all of the other state functions in Table 4.4 as functions of T and P . It is shown that once equations are derived for volume [$V = V(T, P)$] and entropy [$S = S(T, P)$], expressions for the four energy functions readily follow. Once all of the functions have been expressed in terms of (T, P) , conversion to other pairs of independent variables, e.g., express $H = H(V, S)$, requires no mathematics beyond algebra.

4.2.1 ENTROPY AND VOLUME RELATIONS TO T AND P

For every simple substance there exists a relation between its volume, temperature, and pressure, which may be written formally as:

$$V = V(T, P) \quad (4.31)$$

Since these are all state functions, the corresponding differential relation, analogous to the generic Equation 4.17, is

$$dV = M dT + N dP$$

The coefficient relations for M and N in this equation give:

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP$$

The partial derivatives in this equation may be expressed in terms of the experimental variables α and β defined in Equation 4.11 and Equation 4.12.

$$\left(\frac{\partial V}{\partial T} \right)_P = V\alpha \quad \text{and} \quad \left(\frac{\partial V}{\partial P} \right)_T = -V\beta$$

Thus, without any restrictions on the nature of the substance that makes up the system,

$$V = V(T, P) \quad dV = V\alpha dT - V\beta dP \quad (4.32)$$

This equation may be regarded as a differential form of an equation of state. If experimental information is available for the substance in the system for α and β as functions of temperature and pressure, this equation may be integrated (at the very least numerically) to obtain a complete description of the variation of the volume of the system with its temperature and pressure.

Consider now the analogous problem for the entropy function:

$$S = S(T, P) \quad (4.33)$$

The corresponding differential relation is

$$dS = M dT + N dP$$

The coefficients in this equation may be written as partial derivatives so that

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \quad (4.34)$$

The second coefficient, N , has already been evaluated in the consideration of Maxwell relations. Recall Equation 4.26:

$$N = \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P = -V\alpha \quad (4.35)$$

Evaluation of M requires a thermodynamic argument based on the definition of heat capacity.

For any reversible process, the second law connects the heat absorbed with the change in entropy:

$$\delta Q_{\text{rev}} = T dS \quad (3.10)$$

With Equation 4.34

$$\delta Q_{\text{rev}} = T \left[\left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \right]$$

The heat absorbed for a constant pressure process, for which $dP = 0$, may be written

$$\delta Q_{\text{rev},P} = T \left(\frac{\partial S}{\partial T} \right)_P dT_P \quad (4.36)$$

Measurements of the reversible heat absorbed for a constant pressure process are the basis for the experimental evaluation of C_P , the heat capacity at constant pressure,

$$\delta Q_{\text{rev},P} = C_P dT_P \quad (4.13)$$

Comparison of these two expressions for heat absorbed at constant pressure demonstrates that the coefficients of dT_P must be the same quantity in both equations. It is concluded that

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

or,

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad (4.37)$$

Thus, a general differential relation for the variation of entropy with temperature and pressure for any simple system is

$$S = S(T, P) \quad dS = \frac{C_P}{T} dT - V\alpha dP \quad (4.38)$$

If C_P and α are known as functions of temperature and pressure for the system under study, the entropy of the system may be computed by integration of this equation as a function of temperature and pressure. There are no restrictions on the validity of this equation other than the limitations imposed by the simplification that $\delta W' = 0$ for all processes considered in this chapter.

Although Equation 4.32 and Equation 4.38 are sufficient to implement the general procedure shortly to be developed, it is also useful to introduce relations between state functions and the experimental variable, C_V . This brief development is introduced here because it parallels that just presented for C_P . Recall the definition of the heat capacity at constant volume, Equation 4.15:

$$\delta Q_{\text{rev},V} = C_V dT_V \quad (4.15)$$

Variables about which information is given in the process used to determine C_V are the temperature (which is measured) and the volume (which is held constant). The heat absorbed is related to the entropy change of the system. This suggests that the state function $S = S(T, V)$ should be examined. The differential form of this function is

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

For a constant volume process, such as is used in determining C_V , $dV = 0$, and the change in entropy is

$$dS_V = \left(\frac{\partial S}{\partial T}\right)_V dT_V$$

Apply again the second law as embodied in Equation 3.10:

$$\delta Q_{\text{rev},V} = T dS_V = T \left(\frac{\partial S}{\partial T}\right)_V dT_V \quad (4.39)$$

Comparison of coefficients of Equation 4.39 and Equation 4.15 gives

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad (4.40)$$

Thus, C_V may also be expressed in terms of the state functions S and T . Comparison of Equation 4.40 and Equation 4.37 again demonstrates the necessity for specifying the variables that are held constant in taking each derivative. Clearly, since C_P and C_V are not equal to one another, the two entropy derivatives to which they are related must also be different.

4.2.2 ENERGY FUNCTIONS EXPRESSED IN TERMS OF T AND P

The four combined statements of the first and second laws derived in Section 4.1.2 follow directly from the definitions of each of the energy functions and the original version of this statement expressed in terms of dU . The results are summarized here:

$$U = U(S, V); \quad dU = T dS - P dV \quad (4.4)$$

$$H = H(S, P); \quad dH = T dS + V dP \quad (4.6)$$

$$F = F(T, V); \quad dF = -S dT - P dV \quad (4.8)$$

$$G = G(T, P); \quad dG = -S dT + V dP \quad (4.10)$$

Equation 4.32 and Equation 4.38 provide general differential expressions for dV and dS for any system in terms of dT and dP . Conversion of these equations for the energy functions into expressions having T and P as independent variables merely requires substitution for dV or dS where they appear, followed by algebraic simplification. To illustrate, substitute for dS and dV in Equation 4.4:

$$dU = T \left[\frac{C_P}{T} dT - V\alpha dP \right] - P[V\alpha dT - V\beta dP]$$

Collect like terms:

$$U = U(T, P); \quad dU = (C_P - PV\alpha) dT + V(P\beta - T\alpha) dP \quad (4.41)$$

To convert Equation 4.6 for the enthalpy to a function of T and P , substitute for dS ,

$$dH = T \left[\frac{C_P}{T} dT - V\alpha dP \right] + V dP$$

and collect terms:

$$H = H(T, P); \quad dH = C_P dT + V(1 - T\alpha) dP \quad (4.42)$$

Equation 4.8 is similarly easily converted to a function of T and P by substituting for dV :

$$dF = -S dT - P(V\alpha dT - V\beta dP)$$

Collect terms:

$$F = F(T, P); \quad dF = -(S + PV\alpha)dT + PV\beta dP \quad (4.43)$$

The Gibbs free energy function is already expressed in terms of the independent variables T and P in the version originally derived, Equation 4.10.

This collection of all of the state functions expressed in terms of T and P just derived is compiled for quick reference in Table 4.5. Coefficient relations apply to each term in these equations; e.g., in Equation 4.42,

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \quad \text{and} \quad \left(\frac{\partial H}{\partial P}\right)_T = V(1 - T\alpha) \quad (4.44)$$

as do Maxwell relations, e.g.,

$$\left(\frac{\partial C_P}{\partial P}\right)_T = \left(\frac{\partial[V(1 - T\alpha)]}{\partial T}\right)_P \quad (4.45)$$

The coefficients in these equations contain the following factors:

T, P (which are the independent variables specified in any application).

Experimental variables, α, β, C_P , assumed to be available in tables or the literature.

S and V , which can be evaluated as functions of T and P , given α, β and C_P .

Thus, if the initial and final states for a process traversed by a system are specified by their temperature and pressure, knowledge of the values of α, β and C_P permits calculation of all of the changes in state functions accompanying that

TABLE 4.5
Thermodynamic State Functions Expressed in Terms of the Independent Variables Temperature and Pressure

$V = V(T, P)$	$dV = V\alpha dT - V\beta dP$	Equation 4.32
$S = S(T, P)$	$dS = \frac{C_P}{T} dT - V\alpha dP$	Equation 4.38
$U = U(T, P)$	$dU = (C_P - PV\alpha)dT + V(p\beta - T\alpha)dP$	Equation 4.41
$H = H(T, P)$	$dH = C_P dT + V(1 - T\alpha)dP$	Equation 4.42
$F = F(T, P)$	$dF = -(S + PV\alpha)dT + PV\beta dP$	Equation 4.43
$G = G(T, P)$	$dG = -S dT + V dP$	Equation 4.10

process. The power of these equations is demonstrated by the fact that they apply to any system taken through any process.

4.2.3 THE GENERAL PROCEDURE

Translation of a statement of a practical problem into the language of thermodynamics requires the identification of the independent variables (about which information is given), the dependent variable (about which information is sought), and the development of the relationship that connects these variables. The derivation of such relationships is at the heart of the problem. The treatment presented in the previous section yields an exhaustive list of all such relations for any problem in which the independent variables are temperature and pressure (Table 4.5). The procedure for solving the more general problem, in which any pair of state functions (X, Y) may be the independent variables and any third state function Z the variable sought, is laid out in this section. This part of the problem is considered solved (the relation derived) when the coefficients, M and N , have been evaluated in terms of the experimental variables, α, β, C_P (and/or C_V) and the state functions T, P, S , and V , which can always be computed therefrom.

The step-by-step procedure for deriving such relationships is straightforward once the equations in Table 4.5 have been obtained. It requires no higher mathematics than algebra and, indeed, no thermodynamic thinking is involved, since the manipulations are purely mathematical. There are seven steps in the procedure:

1. Identify the variables: $Z = Z(X, Y)$
2. Write the differential form: $dZ = M dX + N dY$
3. Use Table 4.5 to express dX and dY in terms of the variables dT and dP , (this is always possible, since Table 4.5 provides an exhaustive list for all of the state functions we have defined):

$$dZ = M[X_T dT + X_P dP] + N[Y_T dT + Y_P dP]$$

where the coefficients, X_T, X_P, Y_T, Y_P are the coefficients of dT and dP in the expressions for dX and dY in Table 4.5

4. Collect terms:

$$dZ = [M \cdot X_T + N \cdot Y_T] dT + [M \cdot X_P + N \cdot Y_P] dP$$

5. Obtain $Z = Z(T, P)$ from Table 4.5:

$$dZ = Z_T dT + Z_P dP$$

6. The equations listed under steps 4 and 5 are alternate expressions for $Z = Z(T, P)$. Therefore, the coefficients of dT and dP in both equations

are, respectively,

$$\left(\frac{\partial Z}{\partial T_P}\right) \quad \text{and} \quad \left(\frac{\partial Z}{\partial P}\right)_T$$

Equate like terms:

$$M \cdot X_T + N \cdot Y_T = Z_T \quad (4.46a)$$

$$M \cdot X_P + N \cdot Y_P = Z_P \quad (4.46b)$$

7. This is a pair of linear simultaneous equations in M and N and may always be solved for these variables either by elimination of one variable then solution for the other, or, in the worst case, by determinants. The resulting expressions for M and N will certainly be expressed in terms of the experimental variables since all of the terms in Table 4.5 (from which X_T , Y_T , Z_T , X_P , Y_P and Z_P are obtained) are expressed in terms of these variables.

This approach to developing relations among state variables has several advantages over alternative methods. It is mathematically rigorous so that it may be applied with confidence. It requires conscious identification of the independent and dependent variables so that the initial statement of the problem must be clear. The equation that results has general applicability and may be used in any situation, avoiding confusion about which relations are special (e.g., are limited in validity to systems composed of ideal gases or to specific processes). Finally, the path from statement of the problem to its solution is straightforward, eliminating potential confusion about the manipulation of the quantities involved, further fostering confidence in the final result.

Since the mathematics involved in this methodology is only algebra, it is easy to make simple mistakes in computation in following the procedure. Once M and N are evaluated for a given problem, it is strongly recommended that a check of their units be carried out. Most algebraic errors will be clearly exposed with this tactic since the units obtained for M and N in step 7 must agree with the units they are required to have in writing step 2. In this comparison, it is only necessary to represent each thermodynamic quantity in terms of generic units involving only combinations of P , V and T . It will be found to be convenient to represent all measures of energy as having units (PV), then entropy has units (PV/T), heat capacities also have units (PV/T), α has units ($1/T$), β has units ($1/P$).

In the application of the result to the solution of a numerical problem for a specified system, the actual units that are used will be determined primarily by the units that are used in the database from which the experimental information was obtained. Thus, energy functions may be expressed in joules, calories, ergs, liter-atmospheres, Newton-meters, BTU and the like. Such alternative representations of energy may be interconverted at will using the conversion factors reported in

Appendix A. Similarly, heat capacities have units of (energy/mol K) and may be found carrying any of the energy units displayed above. The coefficients of expansion and compressibility may also appear in a variety of units (α as $1/^\circ\text{F}$, e.g., and β as 1 psi^{-1} or 1 MPa^{-1}). All correspond to the generic units listed in the last paragraph.

The general procedure has been stated in the abstract; its application will now be made more concrete with a number of examples. The first set of examples (4.2 to 4.6) illustrate the step-by-step procedure to be followed in order to derive the differential expressions that relate a specific dependent variable to a pair of independent variables. Later examples will apply this procedure as a module in the overall problem that begins with a verbal statement of the situation and ends with a numerical result.

EXAMPLE 4.2

Relate the entropy of a system to its temperature and volume.

1. Identify the variables: $S = S(T, V)$
2. Write the differential form: $dS = M dT + N dV$
3. Convert dV , using Table 4.5:

$$dS = M dT + N(V\alpha dT - V\beta dP)$$

4. Collect terms: $dS = (M + NV\alpha)dT - NV\beta dP$
5. Obtain $S = S(T, P)$ from Table 4.5:

$$dS = [C_P/T]dT - V\alpha dP$$

6. Compare coefficients: $M + NV\alpha = C_P/T$

$$-NV\beta = -V\alpha$$

7. Solve this pair of equations for M and N :

$$N = \left(\frac{\partial S}{\partial V}\right)_T = \frac{\alpha}{\beta}$$

$$M = \left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} \left(C_P - \frac{TV\alpha^2}{\beta} \right)$$

Check the units. From step 2, $M dT$ must have the same units as dS , i.e., (PV/T). Thus M has units (PV/T^2). This checks with the units for the value of M derived in step 7. In particular, for the second term in the brackets the units are $(TV(1/T)^2)/(1/P) = PV/T$; multiplication by the factor $(1/T)$ outside the brackets yields the correct units. $N dP$ also has units of (PV/T). Thus, N has units (P/T). Substituting the units for α and β gives for $N [(1/T)/(1/P)] = P/T$.

Thus, entropy as a function of temperature and volume is given by

$$dS = \frac{1}{T} \left(C_P - \frac{TV\alpha^2}{\beta} \right) dT + \frac{\alpha}{\beta} dV \quad (4.47)$$

Incidentally, this result may be used to derive the general relation that exists between C_P and C_V mentioned in Section 4.1.2. By inspection, the coefficient of dT in this equation is

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} \left(C_P - \frac{TV\alpha^2}{\beta}\right)$$

It was shown [Equation 4.40] that this coefficient is related to C_V

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

Thus,

$$C_V = C_P - \frac{TV\alpha^2}{\beta} \quad (4.48)$$

Accordingly, if either heat capacity has been measured for a system and α and β are known, the other may be calculated. Since all factors in the second term on the right-hand side are positive C_V is always smaller than C_P .

EXAMPLE 4.3

Relate the entropy of a system to its pressure and volume.

1. Identify the variables: $S = S(P, V)$
2. Write the differential form: $dS = M dP + N dV$
3. Convert dV , using Table 4.5:

$$dS = M dP + N(V\alpha dT - V\beta dP)$$

4. Collect terms:

$$dS = NV\alpha dT + (M - NV\beta)dP$$

5. Obtain $S = S(T, P)$ from Table 4.5:

$$dS = [C_P/T]dT - V\alpha dP$$

6. Compare coefficients: $NV\alpha = C_P/T$

$$M - NV\beta = -V\alpha$$

7. Solve this pair of equations for M and N :

$$N = \left(\frac{\partial S}{\partial V}\right)_P = \frac{C_P}{TV\alpha}$$

$$M = \left(\frac{\partial S}{\partial P}\right)_V = \left(\frac{C_P\beta}{T\alpha} - V\alpha\right)$$

Check the units. For M : $[V/T] = [(PV/T)(1/P)/(T/T) = V(1/T)]$
For N : $[P/T] = [(PV/T)/(TV/T)] = P/T$
The units check. Thus, the required relation is

$$dS = \left(\frac{C_P\beta}{T\alpha} - V\alpha\right)dP + \frac{C_P}{TV\alpha}dV \quad (4.49)$$

EXAMPLE 4.4

Find the relationship that would be needed to compute the change in Helmholtz free energy when the initial and final states are specified by their pressure and volume.

1. Identify the variables: $F = F(P, V)$
2. Write the differential form: $dF = M dP + N dV$
3. Convert dV , using Table 4.5: $dF = M dP + N(V\alpha dT - V\beta dP)$
4. Collect terms: $dF = NV\alpha dT + (M - NV\beta)dP$
5. Obtain $F = F(T, P)$ from Table 4.5:

$$dF = -(S + PV\alpha) dT + PV\beta dP$$

6. Compare coefficients: $NV\alpha = -(S + PV\alpha)$.

$$M - NV\beta = PV\beta$$

7. Solve this pair of equations for M and N :

$$N = \left(\frac{\partial F}{\partial V}\right)_P = -\left(\frac{S}{V\alpha} + P\right)$$

$$M = \left(\frac{\partial F}{\partial P}\right)_V = -\frac{S\beta}{\alpha}$$

Check the units. For M : $V = (PV/T)(1/P)/(1/T) = V$
For N : $P = [(PV/T)/(V/T) + P] = P$.
The units check. Thus, the required relation is

$$dF = -\frac{S\beta}{\alpha}dP - \left(\frac{S}{V\alpha} + P\right)dV \quad (4.50)$$

EXAMPLE 4.5

Express the change in enthalpy as a function of volume and entropy.

1. Identify the variables: $H = H(S, V)$
2. Write the differential form: $dH = M dS + N dV$

3. Convert both dS and dV , using Table 4.5:

$$dH = M[(C_P/T)dT - V\alpha dP] + N(V\alpha dT - V\beta dP)$$

4. Collect terms:

$$dH = [M(C_P/T) + NV\alpha]dT - [MV\alpha + NV\beta]dP$$

5. Obtain $H = H(T, P)$ from Table 4.5:

$$dH = C_P dT + V(1 - T\alpha)dP$$

6. Compare coefficients: $MC_P/T + NV\alpha = C_P$

$$-MV\alpha - NV\beta = V(1 - T\alpha)$$

7. Solve this pair of equations for M and N :

Solution of this pair of equations is a nontrivial exercise in algebra but it is only algebra.

Determinants might be used or substitution. The simplest approach in this case follows: Multiply the top equation by β and the bottom by α :

$$\begin{aligned} MC_P\beta/T + NV\alpha\beta &= C_P\beta - MV\alpha^2 \\ -NV\alpha\beta &= V\alpha(1 - T\alpha) \end{aligned}$$

Add the equations: the term involving N drops out.

$$M[C_P\beta/T - V\alpha^2] = C_P\beta + V\alpha(1 - T\alpha)$$

This result may be simplified by applying Equation 4.48. (It is usually true that if one of the independent variables is volume, expression of the coefficients in terms of C_V rather than C_P will give a result that is algebraically simpler.)

$$M \frac{\beta}{T} \left(C_P - \frac{TV\alpha^2}{\beta} \right) = \beta \left(C_P - \frac{TV\alpha^2}{\beta} + \frac{V\alpha}{\beta} \right)$$

or

$$M \frac{\beta}{T} C_V = \beta \left(C_V + \frac{V\alpha}{\beta} \right)$$

Thus,

$$M = \left(\frac{\partial H}{\partial S} \right)_V = T \left(1 + \frac{V\alpha}{\beta C_V} \right)$$

Substitute this result for M into the original version of the first equation

$$T \left(1 + \frac{V\alpha}{\beta C_V} \right) \frac{C_P}{T} + NV\alpha = C_P$$

Solve for N :

$$N \equiv \left(\frac{\partial H}{\partial V} \right)_S = - \frac{C_P}{\beta C_V}$$

Check the units. For $M : T = T\{1 + V(1/T)/[(PV/T)(1/P)]\}$

For $N : P = (PV/T)/[(PV/T)(1/P)]$

Thus, the differential expression for $H = H(S, V)$ is

$$dH = T \left(1 + \frac{V\alpha}{C_V\beta} \right) dS - \frac{C_P}{C_V\beta} dV \quad (4.51)$$

EXAMPLE 4.6

Derive an expression for the increase in temperature for a process in which the volume of the system is changed at constant entropy. The variable about which information is sought is T ; information is given about S and V .

1. Identify the variables: $T = T(S, V)$.

This case differs from those presented above because the dependent variable, T , is one of the variables that we have chosen as an independent variable in developing the arsenal of relations contained in Table 4.5. In such cases rearrange the governing equation so that T is one of the *dependent* variables:

$$S = S(T, V)$$

2. Find the differential relation:

$$dS = M dT + N dV$$

3. Evaluate M and N . Then solve the resulting equation for dT . The relation $S = S(T, V)$ was derived in Example 4.2. Combine Equation 4.47 and Equation 4.48:

$$dS = \frac{C_V}{T} dT + \frac{\alpha}{\beta} dV \quad (4.52)$$

4. Rearrange to solve for dT :

$$dT = \frac{T}{C_V} dS - \frac{T\alpha}{C_V\beta} dV \quad (4.53)$$

From the statement of the problem for the process considered $dS = 0$. Thus, for this *isentropic* process,

$$dT_S = -\frac{T\alpha}{C_V\beta}dV_S$$

If the experimental variables are known for the system integration of this equation from the initial to the final volume will yield the change in temperature.

4.2.4 APPLICATION TO AN IDEAL GAS

The gaseous state of matter is frequently encountered in systems of practical importance. Interaction with gases may lead to degradation through oxidation or hot corrosion. The vapor state may provide a medium for controlled addition of material to a system, as in nitriding or carburization in heat treatment or thin film deposition in processing microelectronic devices. Some chemical reactions may be more closely controlled in the vapor state. The apparatus for the description of mixtures of gases, equilibrium between solids or liquids and their vapors and reactions in gases, is developed in later chapters. Applications in this section are limited to *unary* gases.

The *ideal gas model* provides a description of these gaseous systems that is adequate for many practical purposes. The *equation of state* for an ideal gas, i.e., an algebraic equation that relates volume to temperature and pressure, was established through experimental observation of the behavior of gases by the early 19th century. This most important equation in the description of the behavior of gases is

$$PV = nRT \quad (4.54)$$

where P , V and T are as defined previously. R is the gas constant, determined experimentally to be:

$$\begin{aligned} R &= 8.314 \text{ (J/mol K)} = 1.987 \text{ (Cal/mol K)} = 0.08206 \text{ (l-atm/mol K)} \\ &= 82.06 \text{ (cc-atm/mol K)} \end{aligned} \quad (4.55)$$

and n is the number of moles of the gas in the system. If this equation is used to describe a system containing 1 mol of substance, then $n = 1$ and

$$PV = RT \quad (4.56)$$

where V may be interpreted as the *molar volume* of the gas (volume occupied by 1 mol).

The experimental variables may be computed for an ideal gas as follows. Apply the definition of the volume coefficient of thermal expansion, Equation 4.11,

$$\alpha(\text{ideal gas}) = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{R \frac{T}{P}} \left[\frac{\partial}{\partial T} \left(R \frac{T}{P} \right) \right]_P = \left(\frac{P}{RT} \right) \left(\frac{R}{P} \right) = \frac{1}{T} \quad (4.57)$$

The coefficient of compressibility, Equation 4.12,

$$\beta(\text{ideal gas}) = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\left(\frac{1}{RT} \right) \left[\frac{\partial}{\partial P} \left(\frac{RT}{P} \right) \right]_T = -\frac{P}{RT} \left(-\frac{RT}{P^2} \right) = \frac{1}{P} \quad (4.58)$$

The kinetic theory of gases demonstrates that the heat capacity of an ideal gas is independent of temperature and pressure, but depends upon the number of atoms and their configuration in each gas molecule (see Chapter 6). The relation between C_P and C_V expressed for a general system in Equation 4.48 is particularly simple for an ideal gas since the factor

$$\frac{TV\alpha^2}{\beta} = T \left(R \frac{T}{P} \right) \left(\frac{1}{T} \right)^2 \left(\frac{1}{P} \right) = R$$

Thus, for an ideal gas,

$$C_V = C_P - R \quad (4.59)$$

For a *monatomic* gas (each gas molecule is just a single atom) it is found that

$$C_V(\text{monatomic ideal gas}) = \frac{3}{2}R \quad (4.60)$$

Note that C_V has the same units as R . Insert this value into Equation 4.59 to obtain the corresponding value for C_P :

$$C_P(\text{monatomic ideal gas}) = \frac{3}{2}R + R = \frac{5}{2}R \quad (4.61)$$

An important simplification in the thermodynamic behavior of an ideal gas may be obtained by considering the relation between internal energy and temperature and pressure, $U = U(T, P)$. From Table 4.5,

$$U = U(T, P); \quad dU = (C_P - PV\alpha)dT + V(P\beta - T\alpha)dP \quad (4.41)$$

Apply Equation 4.57 and Equation 4.58 to evaluate the coefficient of dP for an ideal gas:

$$V(P\beta - T\alpha) = V\left[P\left(\frac{1}{P}\right) - T\left(\frac{1}{T}\right)\right] = 0$$

The coefficient of dT may be simplified by evaluating α :

$$C_P - PV\alpha = C_P - PV\left(\frac{1}{T}\right) = C_P - R = C_V$$

Thus, for an ideal gas, Equation 4.41 becomes

$$dU(\text{ideal gas}) = C_V dT + 0dP = C_V dT$$

For any finite change in state from an initial condition given by (T_1, P_1) to a final state (T_2, P_2) , the change in internal energy may be obtained by integrating this equation. This integration is simplified because C_V is a constant for an ideal gas. Thus, for any change in state of a monatomic ideal gas,

$$\Delta U(\text{ideal gas}) = C_V(T_2 - T_1) = \frac{3}{2}R(T_2 - T_1) \quad (4.62)$$

It is concluded that *the internal energy of an ideal gas is a function only of its temperature*. This results from the observation that the coefficient of dP in Equation 4.41 is 0; this is true only for ideal gases and for no other substances. The change in internal energy of an ideal gas for any process can, without exception, be computed from Equation 4.62.

A similar result may be obtained for the enthalpy function. Recall Equation 4.42 from Table 4.5.

$$H = H(T, P); \quad dH = C_P dT + V(1 - T\alpha)dP \quad (4.42)$$

For an ideal gas, the coefficient of dP is found to be

$$V(1 - T\alpha) = V\left[1 - T\left(\frac{1}{T}\right)\right] = 0$$

and Equation 4.42 becomes

$$dH(\text{ideal gas}) = C_P dT + 0dP = C_P dT$$

Integration gives, for a finite change in state:

$$\Delta H(\text{ideal gas}) = C_P(T_2 - T_1) = \frac{5}{2}R(T_2 - T_1) \quad (4.63)$$

from which it is seen that the change in enthalpy of an ideal gas for any process depends only upon the initial and final temperature of the system and no other state function. This unusual result is valid only for an ideal gas because the value of the coefficient of dP is zero.

These results demonstrate that if an ideal gas is subject to any arbitrary process that takes it from state A to state B, the change in internal energy and enthalpy may be computed if the initial and final temperatures are either given or may be computed from the information given. Since U and H are state functions, these results hold for any process connecting the initial and final states, whether reversible or irreversible.

The next series of examples (Example 4.7 to Example 4.11) applies the general procedure and the experimental variables just evaluated to make thermodynamic calculations for processes described for a *monatomic ideal gas*.

EXAMPLE 4.7

Compute the change in entropy when 1 mol of an ideal gas initially at 298 K and one atmosphere pressure is isothermally compressed to 1000 atm.

Identify the variables: $S = S(T, P)$

The differential form for this relationship for a general substance is contained in Table 4.5 since the independent variables are T and P .

$$dS = \frac{C_P}{T} dT - V\alpha dP \quad (4.38)$$

For the problem at hand, $dT = 0$. The coefficient of dP may be evaluated for an ideal gas by applying Equation 4.57 and Equation 4.58

$$dS_T = -V\alpha dP_T = -\left(R\frac{T}{P}\right)\left(\frac{1}{T}\right)dP_T = -\frac{R}{P}dP_T$$

This is the change in entropy for each infinitesimal step in the process. The change in entropy for the whole process is the *integral* of dS_T : from the initial to the final pressure:

$$\begin{aligned} \Delta S_T &= \int_{P_1}^{P_2} \left(-\frac{R}{P}\right) dP = -R \ln P \Big|_{P_1}^{P_2} = -R[\ln P_2 - \ln P_1] \\ \Delta S_T(\text{ideal gas}) &= -R \ln \frac{P_2}{P_1} \end{aligned} \quad (4.64)$$

This expression gives the change in entropy when a monatomic ideal gas experiences a change in pressure at constant temperature. For the current example, $P_1 = 1$ atm and $P_2 = 1000$ atm; thus

$$\Delta S_T = -(8.314 \text{ J/mol K}) \ln(1000/1) = -57.4 \text{ J/mol K}$$

The next example introduces the notion of an *adiabatic* process. Imagine a system enclosed in a thermally insulating jacket. Then whatever processes occur in

the system, no heat flows across its boundary. Processes that occur in such a system for which $\delta Q = 0$, whether reversible or irreversible, are called *adiabatic*. If, in addition, the process considered is carried out reversibly then, since $\delta Q_{\text{rev}} = T dS$ and $\delta Q = 0$, it follows the $dS = 0$ for each infinitesimal step. Thus, adiabatic, reversible processes are isentropic, i.e., occur at constant entropy. (This conclusion is not valid for an irreversible adiabatic process since entropy is produced within the system.)

EXAMPLE 4.8

One mole of an ideal gas initially at temperature T_1 and occupying volume V_1 is compressed reversibly and adiabatically to a final volume V_2 . Compute the final temperature, T_2 of the system.

Identify the variables: $T = T(S, V)$

This problem was previously treated for the general case in Example 4.6, yielding Equation 4.52:

$$dT = \frac{T}{C_V} dS - \frac{T\alpha}{C_V\beta} dV \quad (4.52)$$

Since the process under study is *isentropic*, $dS = 0$ and

$$dT_S = -\frac{T\alpha}{C_V\beta} dV_S \quad (4.65)$$

For an ideal gas $\alpha = 1/T$ and $\beta = 1/P$:

$$dT_S = -\frac{T\left(\frac{1}{T}\right)}{C_V\left(\frac{1}{P}\right)} dV_S = -\frac{P}{C_V} dV_S$$

Eliminate P through the equation of state:

$$dT_S = -\frac{\left(\frac{RT}{V}\right)}{C_V} dV_S$$

Separate the variables and integrate from the initial to the final state:

$$\int_{T_1}^{T_2} \frac{dT}{T} = -\int_{V_1}^{V_2} \frac{R}{C_V} \frac{dV}{V}$$

$$\ln\left(\frac{T_2}{T_1}\right) = -\frac{R}{C_V} \ln\left(\frac{V_2}{V_1}\right) = \ln\left(\frac{V_2}{V_1}\right)^{\left(-\frac{R}{C_V}\right)}$$

Two logarithms are equal if their arguments are equal:

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{\left(-\frac{R}{C_V}\right)} = \left(\frac{V_1}{V_2}\right)^{\left(\frac{R}{C_V}\right)}$$

Thus, the final temperature at the end of the reversibly adiabatic compression is

$$T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\left(\frac{R}{C_V}\right)} \quad (4.66)$$

Note that if V_2 is larger than V_1 , T_2 is smaller than T_1 ; if a gas expands adiabatically, its temperature drops. This phenomenon is the basis for some refrigeration cycles. Similarly, an adiabatic compression of the gas raises its temperature; thus a bicycle pump gets warm as the tire is inflated. Equation 4.65 shows that this phenomenon is general, for all substances. The minus sign on the right-hand side of this equation implies that the temperature change and volume change are in the opposite direction for any reversible adiabatic process.

Equation 4.66, the adiabatic equation for an ideal gas, may also be expressed in terms of relations of T to P or P to V simply by applying the equation of state.

$$T_2 = T_1 \left[\frac{\left(\frac{RT_1}{P_1}\right)}{\left(\frac{RT_2}{P_2}\right)} \right]^{\left(\frac{R}{C_V}\right)}$$

Algebraic manipulation of this equation simplifies to:

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\left(\frac{R}{C_P}\right)} \quad (4.67)$$

which makes use of the previous result that $C_V = C_P - R$ for an ideal gas, Equation 4.59. A similar substitution and manipulation yields the adiabatic relationship expressed in terms of P and V :

$$P_2 = P_1 \left(\frac{V_1}{V_2}\right)^{\left(\frac{C_P}{C_V}\right)} \quad (4.68)$$

These three relationships all describe the same process; the reversible adiabatic compression of an ideal gas; they simply use different variables to describe the path.

The "free expansion" of an ideal gas is a favorite homework problem in every thermodynamic text. Picture a system, Figure 4.3a, with an internal partition separating its volume into two equal parts. The partition contains a valve that may be opened as desired. The whole system is a rigid, thermally insulated box so that processes that occur within it are *adiabatic* and no work can be exchanged with the surroundings. Initially, the valve is closed and one side of the system is evacuated; the other contains 1 mol of an ideal gas at some temperature, T_1 . The valve is then opened and the gas expands freely and irreversibly into the evacuated side of the chamber, Figure 4.3b.

Since the walls of the container do not move during this process, no work is done on the surroundings by the expanding gas: $\delta W = 0$. Since the system is adiabatic, no heat is exchanged with the surroundings: $\delta Q = 0$. During this process the system is *isolated* from its surroundings: no exchanges of any kind occur. Since no transfers occur between system and surroundings, the contribution to the entropy change due to exchanges with the surroundings is zero. Thus, whatever change in entropy occurs in the gas as it expands must be *entropy production* arising from the irreversible nature of the process which evidently occurs far from equilibrium. According to the second law, this entropy production and thus the change in entropy of the system must be *positive*. The problem set out requires the computation of the entropy production for an irreversible process.

This irreversible process is complex: during the expansion, pressure and temperature gradients exist within the gas, heat and mass flows occur, and turbulent conditions may even obtain. No information is supplied that would permit estimation of these complex details in the evolution of the system toward its final state. How then can the entropy produced be computed?

Recognize that entropy is a state function. Thus, the change in entropy for this complex irreversible process is exactly the same as that for the simplest reversible process that can be imagined that connects the initial and final states. The initial state is known: its volume and temperature (V_1, T_1) are specified. The volume of the final state is also known since the gas fills the whole container and the two compartments have the same volume: thus $V_2 = 2V_1$. To complete the specification of the final state, its temperature must be determined.

Recall that the system is isolated during this process: $\delta Q = \delta W = 0$. Thus, according to the first law of thermodynamics, the internal energy of the system, U , cannot change during the process, $\Delta U = 0$. Since the gas is ideal, the internal energy is determined by its temperature, Equation 4.58. Since the internal energy of the initial and final states is the same, the final temperature must be the same as the initial temperature. Thus, while the temperature distribution may be broad and time dependent during the process, the final temperature of the system when it comes to rest is uniform and must also be T_1 . The simplest process that can be visualized that connects the initial state (T_1, V_1) and final state ($T_1, V_2 = 2V_1$) in this system is thus a reversible, isothermal expansion from V_1 to $2V_1$.

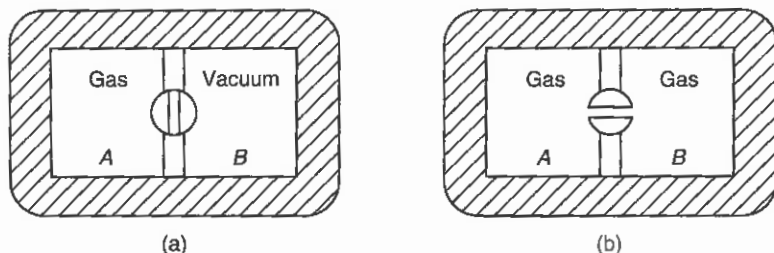


FIGURE 4.3 System illustrating the free expansion of an ideal gas. Initially the gas is contained in chamber A; chamber B is evacuated (a). The valve is opened and the gas expands irreversibly ("freely") to fill both chambers (b).

EXAMPLE 4.9

Compute the change in entropy when 1 mol of an ideal gas expands freely to twice its volume.

Identify the variables: $S = S(T, V)$

Refer to Example 4.6, Equation 4.52:

$$dS = \frac{C_v}{T} dT + \frac{\alpha}{\beta} dV \quad (4.52)$$

Set $dT = 0$ for the isothermal reversible process considered and evaluate α and β for an ideal gas:

$$dS_T = \frac{\alpha}{\beta} dV_T = \frac{1}{T} \frac{1}{\left(\frac{1}{P}\right)} dV_T = \frac{P}{T} dV_T = \frac{R}{V} dV_T$$

Integrate from the initial to the final state:

$$\Delta S_T = \int_{V_1}^{V_2} \frac{R}{V} dV = R \ln\left(\frac{V_2}{V_1}\right) = R \ln\left(\frac{2V_1}{V_1}\right)$$

$$\Delta S_T = R \ln 2 = 5.76 \frac{\text{J}}{\text{mol K}}$$

In this reversible isothermal process the entropy production is zero and the entropy change computed is completely due to heat transfer across the boundary of the system. In the irreversible process illustrated in Figure 4.3, and connecting the same two end states, the entropy change is completely due to entropy production in the system; there is no entropy transferred across the boundary. The change in entropy for the reversible isothermal process is identical to that for the irreversible free expansion in an isolated system because the initial and final states are the same and entropy is a state function. Thus, the entropy produced in the free expansion of an ideal gas to twice its initial volume is positive, as required by the second law and is equal to $+5.76 \text{ J/mol K}$.

The heat absorbed and work done on a system may be computed for any reversible process by integrating $T dS$ or $-P dV$ along the path specified by the sequence of states that defines the process. In the general case this integration is a line integral along a curve that mathematically describes the process. This integration is simplified if one of the variables describing the state of the system is held constant. Example 4.10 illustrates this application of the general procedure.

EXAMPLE 4.10

Derive expressions for the heat absorbed by the system for each of the following classes of reversible processes for 1 mol of an ideal gas:

- Isothermal change in pressure.
- Isobaric change in volume.
- Isochoric (constant volume) change in temperature.

Since the variables sought are process variables, the paths must be specified. Statements 1 to 3 specify paths for three different processes. The heat absorbed in each case is evaluated through $\delta Q_{\text{rev}} = T dS$.

a. Relationship required: $S = S(T, P)$, Equation 4.38

$$dS = \frac{C_P}{T} dT - V\alpha dP$$

Process is isothermal: set $dT = 0$: $dS_T = -V\alpha dP_T$

$$dS_T = -\left(\frac{RT}{P}\right)\left(\frac{1}{T}\right)dP_T = -\frac{R}{P}dP_T$$

The heat absorbed:

$$\delta Q_{\text{rev},T} = T dS_T = -\frac{RT}{P} dP_T$$

Integrate:

$$Q_{\text{rev},T} = -RT \ln\left(\frac{P_2}{P_1}\right) \quad (4.69)$$

b. Relationship required: $S = S(P, V)$, Equation 4.49

$$dS = \left(\frac{C_P\beta}{T\alpha} - V\alpha\right)dP + \left(\frac{C_P}{TV\alpha}\right)dV \quad (4.49)$$

Isobaric change; set $dP = 0$:

$$dS_P = \frac{C_P}{TV\alpha} dV_P$$

Ideal Gas:

$$dS_P = \frac{C_P}{TV\frac{1}{T}} dV_P = \frac{C_P}{V} dV$$

Heat absorbed:

$$\delta Q_{\text{rev},P} = T dS_P = T \frac{C_P}{V} dV_P$$

Substitute for $T = PV/R$:

$$\delta Q_{\text{rev},P} = \left(\frac{PV}{R}\right) \frac{C_P}{V} dV_P = P \frac{C_P}{R} dV_P$$

Integrate; (P is constant):

$$Q_{\text{rev},P} = P \frac{C_P}{R} (V_2 - V_1) \quad (4.70)$$

Note that this result could also be expressed:

$$Q_{\text{rev},P} = C_P(T_2 - T_1)$$

which is consistent with the definition of heat capacity at constant pressure, where C_P is not a function of temperature.

c. Relationship required: $S = S(T, V)$, Equation 4.52.

$$dS = \frac{C_V}{T} dT + \frac{\alpha}{\beta} dV \quad (4.52)$$

Isochoric: set $dV = 0$:

$$dS_V = \frac{C_V}{T} dT_V$$

The heat absorbed:

$$\delta Q_{\text{rev},V} = T dS_V = T \frac{C_V}{T} dT_V = C_V dT_V$$

Integration gives:

$$Q_{\text{rev},V} = C_V(T_2 - T_1)$$

which is consistent with the definition of heat capacity at constant volume, where C_V is not a function of temperature. This result could also be derived by recognizing that, since for an isochoric process $dV = 0$, $\delta W = 0$, so that $\delta Q = dU_V$. Integration gives the result: $\Delta U_V = Q$. According to Equation 4.62, since the internal energy of an ideal gas depends only upon its temperature, for any process, $\Delta U = C_V(T_2 - T_1)$.

EXAMPLE 4.11

One mole of an ideal gas, initially at 273 K and one atmosphere is contained in a chamber that permits programmed control of its state. Controlled quantities of heat and work are supplied to the system so that its pressure and volume change along a line

given by the equation

$$V = 22.4 \left(\frac{1}{\text{atm}} \right) P$$

Assume the process is carried out reversibly. Compute the heat required to be supplied to the system to take it to a final pressure of 0.5 atmospheres. What is the final temperature of the gas?

Independent variables are P and V ; information is needed about S since the heat absorbed is TdS . Thus, the relation required is $S = S(P, V)$. From Example 4.2, Equation 4.49,

$$dS = \left(\frac{C_P \beta}{T \alpha} = V \alpha \right) dP + \frac{C_P}{TV \alpha} dV \quad (4.49)$$

For an ideal gas, evaluation of α and β yields

$$dS = \frac{C_P}{V} dV + \frac{C_V}{P} dP$$

In order to compute the heat absorbed for an incremental step along the specified path, it is necessary to use the equation describing the path to express one of the independent variables in terms of the other. From the specified path,

$$V = 22.4P \quad \text{and} \quad dV = 22.4 dP$$

Use these expressions for V and dV in the entropy relation just obtained to obtain an expression for an incremental change in entropy along the controlled path,

$$dS(\text{this path}) = \frac{C_V}{P} dP + \frac{C_P}{(22.4P)} (22.4 dP) = (C_V + C_P) \frac{1}{P} dP$$

The heat absorbed for this step is

$$\delta Q_{\text{rev}} = T dS = T(C_V + C_P) \frac{1}{P} dP$$

In order to integrate this equation to obtain the total heat absorbed, it is necessary to relate T to P along this path. Evidently this requires combination of the equation of state with the equation for the path:

$$T(P) = \frac{PV}{R} = \frac{P}{R} (22.4P) = 22.4 \frac{P^2}{R}$$

A check of the units in this result demonstrates that the gas constant, R must be expressed as $R = 0.08206$ (1 atm/mol K) for consistent units. Thus, for the given path the temperature of the system varies with the square of the pressure. Substitute:

$$\delta Q_{\text{rev}} = \left(22.4 \frac{P^2}{R} \right) (C_V + C_P) \frac{1}{P} dP = 22.4(C_V + C_P) \frac{P}{R} dP$$

Integration gives the heat absorbed

$$Q_{\text{rev}} = \int_{P_1}^{P_2} 22.4 \left(\frac{C_V + C_P}{R} \right) P dP = 22.4 \left(\frac{C_V + C_P}{R} \right) \frac{P^2}{2} \bigg|_{P_1}^{P_2}$$

Insert values for C_V and C_P for a monatomic gas, together with the initial and final pressures for the process,

$$Q_{\text{rev}} = 22.4 \left(\frac{\frac{3}{2}R + \frac{5}{2}R}{R} \right) \frac{[(0.5)^2 - (1.0)^2]}{2} = 22.4 \times 4(-0.375)$$

$$Q_{\text{rev}} = -33.6 \text{ l atm} = -3404 \text{ J}$$

The final temperature of the system is the value on the path that corresponds to 0.5 atmospheres of pressure:

$$T_2 = 22.4 \left(\frac{1}{\text{atm}} \right) \frac{(0.5)^2 (\text{atm})^2}{0.08206 \left(\frac{1 \text{ atm}}{\text{mol K}} \right)} = 68.2 \text{ K}$$

The final volume is $V = 22.4 \times 0.5 = 11.2$ l. Evidently in order to lower *both* the pressure and the volume simultaneously, it is necessary to extract a significant quantity of heat from the system.

4.2.5 APPLICATIONS TO SOLIDS AND LIQUIDS

Tables 4.1 to 4.3 surveyed the ranges of values of the experimental variables that are typical for solid and liquids. It is observed that, while α , β and C_P are, in general, functions of temperature, pressure, and composition, for a given material these quantities are not strong functions of the state of the system. For many applications that do not involve the gas phase, particularly when only an estimate of the thermodynamic properties is sought, the assumption that α , β and C_P are constants is a useful approximation. Where precise computations are required, the dependence of these quantities upon T and P must be obtained from the literature or experimentally determined. The examples presented in this section illustrate both precise and approximate calculations for selected thermodynamic state functions so that the magnitude of the errors introduced by these approximations can be assessed.

EXAMPLE 4.12

One mole of nickel initially at 300 K and one atmosphere pressure is taken through two separate processes:

- An isobaric change in temperature to 1000 K.
- An isothermal compression to 1000 atm.

Compare the change in enthalpy of the nickel for these two processes.
The experimental variables for nickel (Appendix B) are:

$$V(300 \text{ K}, 1 \text{ atm}) = 6.60 \left(\frac{\text{cc}}{\text{mol}} \right); \quad \alpha = 40 \times 10^{-6} \left(\frac{1}{T} \right); \quad \beta = 26 \times 10^{-7} \left(\frac{1}{\text{atm}} \right)$$

$$C_p(T) = 11.17 + 37.78 \times 10^{-3} T + \frac{3.18 \times 10^5}{T^2} \left(\frac{\text{J}}{\text{mol K}} \right)$$

Identify the variables: $H = H(T, P)$

Obtain the relationship [Equation 4.42 from Table 4.5]

$$dH = C_p dT + V(1 - T\alpha) dP \quad (4.52)$$

For process (a) $dP = 0$ and the change in enthalpy is

$$\begin{aligned} \Delta H &= \int_{300 \text{ K}}^{1000 \text{ K}} \left(11.17 + 37.78 \times 10^{-3} T + \frac{3.18 \times 10^5}{T^2} \right) dT \\ &= \left[11.17T + 37.78 \times 10^{-3} \frac{T^2}{2} + \frac{3.18 \times 10^5}{-T^1} \right]_{300 \text{ K}}^{1000 \text{ K}} \end{aligned}$$

The second and third terms on the right-hand side of this equation arise from the temperature-dependent contribution to the heat capacity. The first term represents the estimate of ΔH for the process if this temperature-dependent terms were ignored. Evidently, a significant error would be introduced if the temperature-dependent terms were ignored.

For process (b) $dT = 0$ and the change in enthalpy is

$$\Delta H = \int_1^{1000} V(1 - T\alpha) dP$$

If V and α are approximated as constants, they may be factored out of the integral so that

$$\Delta H = V(1 - T\alpha)(P_2 - P_1)$$

$$\Delta H = 6.60 \frac{\text{cc}}{\text{mol}} \left[1 - 40 \times 10^{-6} \frac{1}{T} 300 \text{ K} \right] [1000 - 1] \text{ atm} \frac{8.314 \text{ J}}{82.06 \text{ cc atm}}$$

Since α typically has values in the range of $10^{-5} (1 \text{ K}^{-1})$, the product $T\alpha$ is in general small in comparison to 1. Thus, any second-order contributions to α , e.g., due to its variation with pressure, will certainly be negligible and the factor $[1 - T\alpha]$ may be treated as a constant (i.e., not dependent on pressure) without significant error. The pressure dependence of the molar volume may be expressed to

a first approximation as

$$V(P) = V(P_1)[1 + \beta(P - P_1)]$$

Substitute this result for V in the equation for dH_T

$$dH_T = V(P_1)[1 + \beta(P - P_1)][1 - T\alpha] dP$$

Integrate over the pressure range:

$$\Delta H = \int_{P_1}^{P_2} V(P_1)[1 + \beta(P - P_1)][1 - T\alpha] dP$$

$$\Delta H = V(P_1)(1 - T\alpha) \left[P + \beta \frac{(P - P_1)^2}{2} \right]_{P_1}^{P_2}$$

$$\Delta H = V(P_1)[1 - T\alpha] \left[(P_2 - P_1) + \beta \frac{(P_2 - P_1)^2}{2} \right]$$

Insert the numerical values for the problem at hand:

$$\Delta H = (6514 + 8.5) = 6522 \frac{1 \text{ atm}}{\text{mol K}} = 660.0 + 0.857 = 660.8 \frac{\text{J}}{\text{mol}}$$

where the second term traces to the assumed pressure variation of the molar volume and the first term is identical to that computed approximately earlier in this example. It will be noted that the second term is significant only if the pressure change in the system is extremely large, say 100,000 atm. Thus, for most processes, the assumption that V does not change with pressure yields an approximate result that is within the experimental error of measurement of the precise result.

Comparison of the enthalpy changes for processes (a) and (b) in this example reveals another point that has broad application in the behavior of solids and liquids. Process (a) visualizes a change of a factor of 3 in the absolute temperature; in process (b) the pressure is changed by a factor of 1000. The energy change, here reported as the enthalpy, for process (a) is nonetheless about 25 times larger than for process (b). Thus, for solids and liquids, energy changes associated with thermal influences tend to be much larger than those arising from mechanical influences.

EXAMPLE 4.13

Compute the change in Gibbs free energy of magnesia (MgO) when 1 mol is heated from 298 (room temperature) to 1300 K at one atmosphere pressure. The properties of MgO obtained from Appendix E are:

$$C_p = 48.99 + 3.43 \times 10^{-3} T - \frac{11.34 \times 10^{-5}}{T^2} \left(\frac{\text{J}}{\text{mol K}} \right)$$

$$S_{298}^{\circ} = 26.9 \left(\frac{\text{J}}{\text{mol K}} \right)$$

where S_{298}° is the absolute entropy of MgO at 298 K, obtained by integrating heat capacity data from 0 to 298 K. The variables in the problem:

$$G = G(T, P)$$

From Table 4.5:

$$dG = -S dT + V dP \quad (4.10)$$

In this problem,

$$dP = 0; \quad dG_P = -S dT_P$$

The temperature dependence of S cannot be neglected in this case. Thus, in order to integrate this expression, it is first necessary to develop an expression for the variation of entropy with temperature at constant pressure. Recall again Equation 4.38:

$$dS = \frac{C_P}{T} dT - V \alpha dP \quad (4.38)$$

The condition $dP = 0$ gives:

$$dP = 0; \quad dS_P = \frac{C_P(T)}{T} dT_P$$

Insert the expression for the heat capacity and integrate from 298 K to a variable temperature, T :

$$\int_{298 \text{ K}}^T dS = S(T) - S_{298}^{\circ} = \int_{298 \text{ K}}^T \frac{C_P(T)}{T} dT$$

The absolute value of the entropy at any temperature is thus

$$S(T) = S_{298}^{\circ} + \int_{298 \text{ K}}^T \frac{C_P(T)}{T} dT$$

Insert this expression into

$$\int_{298 \text{ K}}^T dG_P = G(T) - G(298) = \int_{298 \text{ K}}^T -S(T) dT_P$$

to give

$$G(T) - G(298) = \int_{298}^T - \left[S_{298}^{\circ} + \int_{298}^T \frac{C_P(T)}{T} dT \right] dT$$

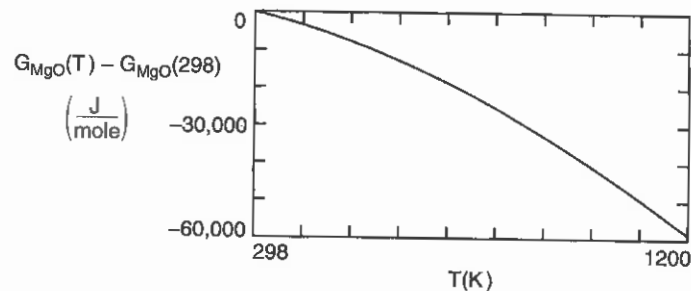


FIGURE 4.4 Variation of Gibbs free energy of MgO with temperature at one atmosphere pressure.

Insert the heat capacity function for MgO and the absolute entropy of MgO at 298 into this equation and perform the indicated double integration. This procedure may be very conveniently carried out in MathCad or a similar mathematical software package. This functional relationship is presented in Figure 4.4.

EXAMPLE 4.14

One mole of copper initially at 700 K and one atmosphere is contained in a thermally insulated jacket. The system is compressed reversibly to a pressure of 10,000 atmospheres. Compute the change in temperature for this reversible adiabatic process. Identify the variables: $T = T(S, P)$

Rearrange (because the independent variable is T)

$$S = S(T, P)$$

Recall this relation from Table 4.5:

$$dS = \frac{C_P}{T} dT - V \alpha dP \quad (4.38)$$

Solve for dT :

$$dT = \frac{T}{C_P} dS + \frac{TV\alpha}{C_P} dP$$

Set $dS = 0$ for this reversible adiabatic process:

$$dT_S = \frac{TV\alpha}{C_P} dP_S$$

Assuming V , α and C_p are constants in the problem, separate the variables:

$$\frac{dT}{T} = \frac{V\alpha}{C_p} dP$$

Integrate:

$$\ln\left(\frac{T_2}{T_1}\right) = \frac{V\alpha}{C_p}(P_2 - P_1)$$

Substitute the properties of copper from Appendix B and compute the result:

$$T_2 = 700 \text{ K} \left[\exp \left(\frac{7.09 \frac{\text{cc}}{\text{mol}} 51 \times 10^{-6} \frac{1}{\text{K}}}{27.3 \frac{\text{J}}{\text{mol K}}} (10,000 - 1) \left(\frac{8.314 \text{ J}}{82.06 \text{ cc atm}} \right) \right) \right]$$

$$T_2 = 709 \text{ K.}$$

EXAMPLE 4.15

This example presents an analog to the illustration of the free expansion of an ideal gas presented in Example 4.9. One mole of pure iron is initially at 300 K and 100,000 atm. The system is contained in a thermally insulating jacket. The pressure is suddenly released; the iron expands irreversibly to a final pressure of one atmosphere. Compute the entropy produced in this irreversible process.

Since for an elastic solid, the volume change is very small, even under extreme hydrostatic pressures such as those considered here, it may be assumed that the work done on the system during this expansion is negligibly different from zero. Since the process is also adiabatic, by the first law the internal energy of the system is constant. Further, since there is essentially no exchange with the surroundings, the entropy flow across the boundary of the system is also negligible. Thus, the change in entropy for the process is virtually all entropy produced inside the system; by the second law, this entropy production must be positive.

The entropy production in this irreversible process may be computed by applying again the familiar strategy. Visualize the simplest reversible process that will connect the same initial and final states. Since entropy is a state function, the change for that process will be the same as that for the irreversible process in the problem. Thus, it is necessary to compute the change in entropy associated with a reversible decompression of 1 mol of iron at constant internal energy.

1. Identify the variables: $S = S(U, P)$.
2. Write the differential form: $dS = M dU + N dP$.
3. Use Equation 4.41 in Table 4.5 to convert dU to a function of T and P :

$$dS = M[(C_p - PV\alpha)dT + V(P\beta - T\alpha)dP] + N dP$$

4. Collect terms:

$$dS = M(C_p - PV\alpha)dT + [MV(P\beta - T\alpha) + N]dP$$

5. Recall Equation 4.38 from Table 4.5:

$$dS = \frac{C_p}{T} dT - V\alpha dP \quad (4.38)$$

6. Compare coefficients

$$M(C_p - PV\alpha) = \frac{C_p}{T}$$

$$MV(P\beta - T\alpha) + N = -V\alpha$$

7. Solve for M and N :

$$M = \left(\frac{\partial S}{\partial U} \right)_P = \frac{C_p}{T(C_p - PV\alpha)}$$

$$N = \left(\frac{\partial S}{\partial P} \right)_U = -\frac{PV(C_p\beta - TV\alpha^2)}{T(C_p - PV\alpha)}$$

The required relation is:

$$dS = \frac{C_p}{T(C_p - PV\alpha)} dU - \frac{PV(C_p\beta - TV\alpha^2)}{T(C_p - PV\alpha)} dP$$

In the problem at hand $dU = 0$ and the change in entropy is

$$dS_U = -\frac{PV(C_p\beta - TV\alpha^2)}{T(C_p - PV\alpha)} dP_U$$

Integration of this equation requires a knowledge of the dependence upon pressure of all of the experimental variables contained in the coefficient of dP_U . However, examination of the numerical values of these quantities shows that the term $PV\alpha$ is small in comparison with C_p , even at the start of the process with $P = 100,000$ atm. The factor in the numerator, $TV\alpha^2$, is even smaller. Thus, to a very good approximation,

$$dS_U = -\frac{PV\beta}{T} dP_U$$

Computation of the change in temperature [based upon $T = T(U, P)$] reveals that the temperature may decrease by about 10 K in this process. This change is small compared with the value of the temperature for the system. If it is also neglected, the entropy produced may be calculated approximately to be:

$$\Delta S = - \left[\frac{\left(7.09 \frac{\text{cc}}{\text{mol}} 6.6 \times 10^{-7} \frac{1}{\text{atm}} \right)}{300 \text{ K}} \right] \frac{1}{2} (1^2 - 100,000^2) (\text{atm})^2$$

$$\Delta S = +2.2 \times 10^{-5} \left(\frac{\text{cc atm}}{\text{mol K}} \right) = +2.2 \times 10^{-6} \left(\frac{\text{J}}{\text{mol K}} \right).$$

4.3 SUMMARY

Thermodynamic relationships may be usefully classified as:

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1. The laws of thermodynamics.
2. Definitions.
3. Coefficient relations.
4. Maxwell relations.
5. Conditions for equilibrium.

The laws of thermodynamics form the physical basis for solving practical problems.

Additional energy functions are defined:

$$H = U + PV; \quad F = U - TS; \quad G = U + PV - TS$$

because they provide measures of energy that are convenient for specific classes of processes. Alternate forms of the combined statements of the first and second laws may be derived for these energy functions:

$$dU = T dS - P dV + \delta W' \quad (4.4)$$

$$dH = T dS + V dP + \delta W' \quad (4.6)$$

$$dF = -S dT - P dV + \delta W' \quad (4.8)$$

$$dG = -S dT + V dP + \delta W' \quad (4.10)$$

A collection of experimental variables is defined:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (4.11)$$

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (4.12)$$

$$\delta Q_{\text{rev},P} = C_P dT_P \quad (4.13)$$

$$\delta Q_{\text{rev},V} = C_V dT_V \quad (4.15)$$

These variables provide complete information about changes in the thermodynamic properties of systems for which $\delta W' = 0$; no other empirical information is required.

Coefficient and Maxwell relations derive from the mathematical properties of differentials of functions of several variables. For any thermodynamic relation between differentials of state functions, these relations may be read by inspection of

the equation:

$$Z = Z(X, Y) \quad (4.16)$$

$$dZ = M dX + N dY \quad (4.17)$$

$$M = \left(\frac{\partial Z}{\partial X} \right)_Y; \quad N = \left(\frac{\partial Z}{\partial Y} \right)_X \quad (4.18)$$

$$\left(\frac{\partial M}{\partial Y} \right)_X = \left(\frac{\partial N}{\partial X} \right)_Y \quad (4.25)$$

A general, rigorous procedure provides an algorithm for deriving the thermodynamic relationship between any dependent variable, Z and any pair of independent variables, (X, Y) . This procedure begins with derivation of functional relationships for every other state function in terms of independent variables, T and P . Expressions for the energy functions are easily derived once relationships for $V = V(T, P)$ and $S = S(T, P)$ are obtained:

$$dV = V\alpha dT - V\beta dP \quad (4.32)$$

$$dS = \frac{C_P}{T} dT - V\alpha dP \quad (4.38)$$

The dependence of the energy functions upon T and P may be derived by insertion of these expressions for dS and dV into the combined statements of the first and second laws reviewed at the beginning of this summary:

$$U = U(T, P); \quad dU = (C_P - PV\alpha)dT + V(P\beta - T\alpha)dP \quad (4.41)$$

$$H = H(T, P); \quad dH = C_P dT + V(1 - T\alpha)dP \quad (4.42)$$

$$F = F(T, P); \quad dF = -(S + PV\alpha)dT + PV\beta dP \quad (4.43)$$

$$G = G(T, P); \quad dG = -S dT + V dP \quad (4.11)$$

These key equations are summarized in Table 4.5. For any given problem with arbitrary variables $Z = Z(X, Y)$ with differential form $dZ = M dX + N dY$ the general procedure uses these equations to convert dX and dY to differential forms involving dT and dP . Then, dZ is written as a function of dT and dP . The resulting pair of equations for dZ are alternate expressions for $Z = Z(T, P)$. Corresponding coefficients must therefore be equal. Equating corresponding coefficients yields two linear simultaneous equations in M and N . Evaluation of M and N in terms of experimental variables completes the derivation of the required relationship.

To obtain a numerical result for a given practical problem which seeks the change in Z for initial and final states specified by values of X and Y , it is necessary to

obtain numerical values for the experimental variables in M and N and integrate, first over dX , then over dY . If the problem at hand requires the evaluation of a process variable involving dZ (either $\delta Q = T dS$ or $\delta W = -P dV$), it is necessary to carry out the integration along the path which must be described explicitly as a relation between X and Y .

A variety of examples illustrate the procedure. It is demonstrated that its application is particularly simple for an ideal gas, defined by the equation of state:

$$PV = RT \quad (4.56)$$

and a fixed value of heat capacity:

$$C_V = \frac{3}{2}R; \quad C_P = C_V + R = \frac{5}{2}R$$

for a monatomic gas. These examples demonstrate that the internal energy and the enthalpy of an ideal gas are each a function only of temperature:

$$\Delta U = C_V(T_2 - T_1) \quad (4.62)$$

$$\Delta H = C_P(T_2 - T_1) \quad (4.63)$$

A final set of examples applies to condensed phases demonstrating the generality of the procedure.

HOMEWORK PROBLEMS

Problem 4.1. Write out the combined statements of the first and second laws for the energy functions, $U = U(S, V)$, $H = H(S, P)$, $F = F(T, V)$ and $G = G(T, P)$. Assume $\delta W'$ is zero:

- Write out all eight coefficient relations.
 - Derive all four Maxwell relations.
- for these equations.

Problem 4.2. Derive the ratio relation Equation 4.30:

$$\left(\frac{\partial Z}{\partial X}\right)_Y \left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X = -1$$

[Hint: Begin with the differential form of $Z = Z(X, Y)$; solve for dX ; write the differential form of $X = X(Y, Z)$; compare coefficients.]

Problem 4.3. The molar volume of Al_2O_3 at 25°C and 1 atm is 25.715 cc/mol . Its coefficient of thermal expansion is $26 \times 10^{-6} \text{ K}^{-1}$ and the coefficient of

compressibility is $8.0 \times 10^{-7} \text{ atm}^{-1}$. Estimate the molar volume of Al_2O_3 at 400°C and 10 kbars pressure ($10 \times 10^3 \text{ atm}$).

Problem 4.4. Compare the entropy changes for the following processes:

- One gram atom of nickel is heated at one atmosphere from 300 to 1300 K.
- One gram atom of nickel at 300 K is isothermally compressed from 1 atm to 100 kbars.
- One mole of zirconia is heated at one atmosphere from 300 to 1300 K.
- One mole of zirconia at 300 K is isothermally compressed from 1 atm to 100 kbars. (Use $V = 22.0 \text{ (cc mol}^{-1}\text{)}$ and $\alpha = 10 \times 10^{-6} \text{ K}^{-1}$.)
- One mole of oxygen is heated at one atmosphere from 300 to 1300 K. (Assume O_2 is an ideal gas with $C_P = 7/2R$.)
- One mole of oxygen at 300 K is isothermally compressed from 1 atm to 100 kbars.

What general qualitative conclusions do you draw from these calculations?

Problem 4.5. Express the results obtained for parts (c) and (d) of Problem 4.4 in values *per gram atom* of ZrO_2 . (Each mole of zirconia contains three gram atoms of its elements: one gram atom of zirconium and two of oxygen.) How does this result influence the conclusions you made in the comparisons in Problem 4.4?

Use the *general procedure for deriving relationships in thermodynamics* to solve the remaining problems in this chapter. Begin by identifying explicitly the dependent and independent variables in each case.

Problem 4.6. Compute the change in internal energy when 12 l of argon gas at 273 K and 1 atm is compressed to 6 l with the final pressure equal to 10 atm. Solve this problem in two different ways:

- Apply the general procedure to evaluate $U = U(P, V)$ for an ideal gas and integrate from initial to final (P, V) .
- Use the information given to compute the final temperature of the gas and apply the general relation $\Delta U = C_V \Delta T$.

Assume $C_V = (3/2)R$ for this monatomic gas.

Problem 4.7. Compute and plot the surface that represents the relationship for the entropy of nitrogen gas as a function of temperature and pressure in the (P, T) range from (1 atm, 300 K) to (10 atm, 1000 K). Since nitrogen is diatomic, $C_P = (7/2)R$. Assume it obeys the ideal gas law in this domain.

Problem 4.8. Compute and plot the surfaces that represent the variation with pressure and volume of:

- The internal energy.
- The enthalpy.

of 1 mol of nitrogen gas. Cover the range in (P, V) space from (1 atm, 22.4 l) to (10 atm, 8.2 l). Plot constant energy lines on the surfaces. Assume it behaves ideally.

Problem 4.9. Evaluate the partial derivative

$$\left(\frac{\partial H}{\partial G}\right)_S$$

in terms of experimental variables.

Problem 4.10. Derive the relationship that describes the dependence of Helmholtz free energy upon entropy and temperature. Design an experiment which would require this relationship in analyzing the results.

Problem 4.11. Demonstrate that the change in a state function for a process is independent of the path by calculating the change in Gibbs free energy for two processes that change the state of 1 mol of a monatomic ideal gas from (298 K, 1 atm) to (600 K, 1000 atm):

- Process A:* heat the gas at 1 atm from 298 K to 600 K, then compress it at 600 K from 1 atm to 1000 atm to arrive at the final state; (600 K, 1000 atm).
- Process B:* compress the gas from 1 atm to 1000 atm at 298 K, then heat the gas at 1000 atm from 298 K to 600 K to arrive at the final state; (600 K, 1000).

Show that the same result is obtained by applying the definitional relation: $\Delta G = \Delta H - T\Delta S$. (Note that $\Delta(TS) \neq T\Delta S$.) (*Hint:* the absolute entropy in the second step of part (b) contains the pressure term.)

Problem 4.12. A system is designed that permits continuous programmed control of the pressure and volume of the gas that it contains. The system is filled with 1 g atom of helium and brought to an initial condition of one atmosphere and 18 l. It is then reversibly compressed to 12 l along a programmed path given by the relationship

$$V = -2P^2 + 20$$

where P is in atmospheres and V is in liters. Compute:

- The initial and final temperature of the system.
- The heat absorbed by the system.
- The work done by the system.
- The changes in U , H , F , G , and S .

Problem 4.13. Estimate the pressure increase required to impart 1 J of mechanical work in reversibly compressing 1 mol of silver at room temperature. What pressure rise would be required to impart 1 J of work to 1 mol of alumina at room

temperature? For Al_2O_3 take the molar volume to be $25.715 \text{ (cc mol}^{-1}\text{)}$ and $\beta = 8.0 \times 10^{-7} \text{ (atm)}^{-1}$.

Problem 4.14. Compute and plot the surface representing the Gibbs free energy of hydrogen gas as a function of temperature and pressure in the range from (298 K, 10^{-10} atm) to (1000 K, 100 atm). Use (298 K, 1 atm) as the zero point for the calculation. The absolute entropy of H_2 at 298 K and 1 atm is $130.57 \text{ (J mol}^{-1}\text{K}^{-1}\text{)}$; assume that $C_P = 7/2 R \text{ (J mol}^{-1}\text{K}^{-1}\text{)}$ is independent of P and T .

Problem 4.15. Use a mathematics applications program, spreadsheet or computer language to program and plot the generic equations for computing the temperature dependence of enthalpy, entropy, and Gibbs free energy as a function of temperature at one atmosphere pressure. Assume as input the absolute entropy of the substance at 298 K and values of a , b and c in the empirical heat capacity expression

$$C_P = a + bT + \frac{c}{T^2}$$

Use the program to compute H , S and G (relative to their values at 298 K) as functions of temperature at one atmosphere for

- Argon.
- Titanium.
- TiO_2 .

Problem 4.16. Using the bounding values in Tables 4.1 to 4.3, estimate the range of the magnitude of the difference between C_P and C_V for condensed phases.

Problem 4.17. According to Appendix E, the heat of formation of the compound CoO is $-237,700 \text{ J}$. Compute the enthalpy change for this reaction as a function of temperature in the range from 300 to 1000 K. What is the maximum error incurring in this range if it is assumed that ΔH is independent of temperature. (*Hint:* $d(\Delta H) = \Delta C_P(T) dT$.)

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5 Equilibrium in Thermodynamic Systems

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This chapter introduces a general principle that is the basis for determining the internal condition of the most complex kind of thermodynamic system when it reaches its equilibrium state. This general criterion for equilibrium has the same level of importance in the development of thermodynamics as do the laws themselves, as implied in Figure 1.4. It is the foundation that provides the strategy for the calculation equilibrium maps: phase diagrams, chemical equilibria in predominance diagrams without and with electrical effects, the role played by capillarity effects, the chemistry of defects in crystals, as well as the primary results of statistical thermodynamics. These applications of this criterion occupy most of the rest of this text.

Some intuitive notions of equilibrium are first presented; these ideas are then formalized to provide a thermodynamic statement of the criterion that determines when a system that is isolated from its surrounding during its approach to equilibrium has attained its equilibrium state:

In an isolated system, the entropy is a maximum at equilibrium.

This thermodynamic extremum principle (the entropy has an extreme value, a maximum) is then formulated mathematically. A set of equations, called the conditions for equilibrium, that describe the relationships that the internal properties of the isolated system must have when it achieves its equilibrium state are derived from this extremum principle. It is then demonstrated that although these conditions for equilibrium are derived for an isolated system, they are valid for any system at equilibrium whether or not it was isolated during its approach to that final condition.