

# CHAPTER ONE

## An Introduction to Thermodynamics Systems and Processes

### An Overview

Original Objectives. The formal study of thermodynamics has its roots in the industrial revolution, following the construction of the first successful atmospheric steam engines in England: first by Thomas Savery in 1697 and then by Thomas Newcomen in 1712. The word “thermodynamics” arises from the Greek terms representing heat (therme) and power (dynamis), which pretty well describes the efforts of the founders of this discipline. Their original objective was to gain the most power (energy per unit time) from a given amount of energy stored in some fuel (which was typically turned into heat).

The First and Second Laws. The classical study of thermodynamics primarily deals with the concepts of energy, energy transfer, and energy transformation within some material system as the macroscopic parameters of that system change. The formalism of thermodynamics arises primarily from the precise mathematical expression of two very fundamental observations. The first is the observation that energy, as defined in physics, is conserved - it cannot be created or destroyed - it is simply transformed from one form into another. For example, when a stone is dropped from some height, it loses gravitational potential energy as it falls, but the kinetic energy of the stone increases during this process in such a way that the total energy is conserved. In many mechanical processes, however, we observe what appears to be “energy loss” due to friction, air resistance, etc. Careful observation of these situations usually shows that the mechanical energy which has been lost has simply been transformed into thermal energy (what we often call heat energy). The study of thermodynamics has, to a large extent, grown out of our desire to understand the nature of this heat energy and to understand the transformation of mechanical energy into heat energy and vice versa. The second fundamental observation upon which the study of thermodynamics is based is the everyday observation that heat energy flows spontaneously from hot objects to cold objects, and never the other way around.

These two observations, called the first and second laws of thermodynamics, respectively, were not stated in their present form until the 1850's (the first thermodynamics textbook was not written until 1859 by William Rankine, a professor at the University of Glasgow). Many of the early views of thermodynamics were based upon the false assumption that matter contained a substance called “caloric”. This caloric was thought to be a massless substance which filled in the spaces between the “particle of matter” causing the expansion of a material when it became heated. The transfer of heat was simply viewed as the transfer of this caloric from one object to another. From this perspective, one might be able to say that an object “contained” a certain amount of heat. It was not until the mid to late 1700's that people began to notice inconsistencies in the caloric theory. One particular observation which indicated a problem with the caloric theory was the seemingly infinite amount of heat which could be produced when boring a canon. A team of horses was used to bore the hole in a cast iron canon. During this process, water was poured into the bore hole to keep the cast iron canon from overheating. This water would soon come to a boil and water would be continually added to the bore hole as the water boiled off. There seemed to be no limit to the amount of heat energy which could be derived from the boring process. Observing this phenomenon, Count Rumford concluded that the heat energy supplied to the water could not simply be coming from the cast iron, but must be supplied in a continual process by the friction between the boring tool and the canon. That is, the mechanical energy supplied by the horses was being transformed into the thermal energy supplied to the water to change its temperature and to boil the water. With this new perspective, one could no longer say that an object “contains” a certain amount of heat. A proper understanding of the link between mechanical energy and internal energy was crucial to the development of modern thermodynamics.

Internal Energy, Classical and Statistical Thermodynamics. Both the first and second law deal with energy that is transferred from one system to another in the form of heat. This transfer of energy must be related to the energy that is stored in each system. We call this stored energy the internal energy. We now understand that the internal energy of a system is associated with the microscopic motion of the molecules that make up that system. The founding fathers of thermodynamics, however, did not have this model to build upon, and so classical thermodynamics is primarily a study of the changes in the *macroscopic* (large-scale, observable) properties of a system, with internal energy being one of these macroscopic quantities.

Today, we have a somewhat easier job of understanding the basic concepts of thermodynamics, because we have a superior model upon which to build. We now understand that the internal energy of a system is comprised of two separate parts: 1) the kinetic energy of translation, rotation, and vibration, and 2) the potential energy of interaction between the various molecules. For a gas, the rotational and vibrational kinetic energy is

important only for polyatomic molecules. Unlike the translational kinetic energy, these energies are quantized, the rotational kinetic energy being more easily activated than the vibrational. A monatomic gas, however, can be characterized solely on the basis of its translational kinetic energy and the potential energy of interaction between the individual atoms. This internal potential energy is related to the average force of interaction between the individual molecules which constitute the gas. When these molecules are far apart (as in a gas at low pressure), their interaction is negligible. When the molecules approach each other, they repel. In many cases, we can treat a gas as a large number of solid balls which do not interact unless the balls “hit”. If the average distance between molecules is large in comparison to the size of the molecules, the potential energy of the gas can be neglected and the collisions between the particles are considered to be completely elastic collisions. These collisions will simply transfer kinetic energy from one molecule to another in such a way that the molecules will move in a random fashion. The energy associated with this random motion is what we think of as heat energy - unorganized energy. So the random kinetic energy of a gas must somehow be related to the temperature of the gas.

In the case of a solid, we can model the system after a series of balls held together by springs. Again, the individual particles possess both kinetic and potential energies. The potential energy stored in the springs is associated with the amount the springs are compressed or stretched from their equilibrium positions. The kinetic energy is just the energy of back and forth motion of the individual particles. We again associate the random kinetic energy of the individual particles with the temperature of the solid. If enough energy is added to a liquid or solid the binding energy (potential energy) may be overcome and the individual molecules may become free to move around - no longer bound to the other molecules. This constitutes a change in *phase* of the system. The energy required to break these bonds and to initiate the phase change is called the *latent energy* (or *latent heat*) of the material.

Applicability of Thermodynamics Practically every aspect of our lives involves the interaction between matter and energy, and therefore is subject to the study of thermodynamics. Today, one cannot imagine life without refrigeration or electric power generation, both arising from our understanding of thermodynamic principles. All modern transportation is based upon our application of the principles of thermodynamics in gasoline, diesel, and jet engines. Our understanding of how the body utilizes food and stores fat can also be viewed from a thermodynamic point of view. A clearer understanding of thermodynamic principles can help us to understand why frost forms on some windows and not others, why fog forms above a lake in the early morning, and on which side of the bathroom window the moisture will form in winter and in summer.

### Interactions Between Thermodynamic Systems

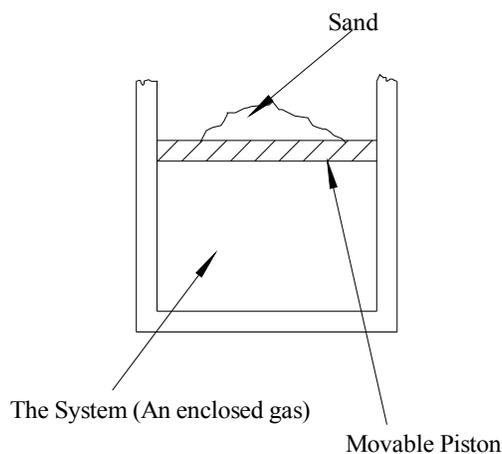
As we begin a thermodynamic analysis of any system, we must first clearly define the system under study and distinguish that system from its surrounding. Only then are we in a position to properly discuss the *interactions* between that system and its surroundings.

Thermodynamic Systems A thermodynamic system is some pre-defined part of our universe which may interact with its surroundings *mechanically, chemically, or thermally*. It is that part of the universe in which we are interested. We may define the system in terms of *a quantity of matter* (a **closed** or **fixed mass** system [in engineering, a **control mass**]), or *a region of space* (an **open** or **fixed volume** system [in engineering, a **control volume**]) chosen for study. The region *outside* the system of interest is called the *surroundings*, and the real or imaginary surface that separates the system from its surroundings is called the *boundary*. The boundary may be *fixed* or *movable*.

One example of a thermodynamic system might be a gas contained inside of a cylinder which is closed off at the top by a movable piston (see Fig. 1.1). This gas is subject to the external atmospheric pressure and to the weight of the piston. If the atmospheric pressure were to increase, the volume of the gas would subsequently decrease, causing the pressure of the gas inside the cylinder to rise. The result of this process is a *mechanical* movement of the piston, and can be considered as work done on the gas to compress it. On the other hand, the gas may be heated by its contact with the outside air, by absorbing radiant energy from the sun, or by being heated with a bunsen burner, causing the gas to expand. Another example of a thermodynamic system might be an iceberg floating in the ocean. This iceberg, which is floating due to the buoyant force of the ocean water on the less dense ice, may be slowly melting as the iceberg extracts heat from the surrounding air and water.

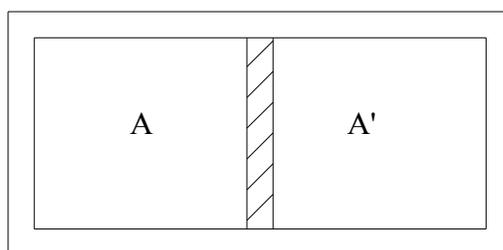
In the chapters which follow we will refer to certain idealized systems: for example 1) a solid block of wood, 2) a container of water, or 3) a gas confined within a container with a movable piston much like that mentioned above. The one we will most often refer to is the gas system of Fig. 1.1. This system will typically be idealized by assuming the piston is *massless and frictionless* and the fitting between the wall of the cylinder and the piston is *air tight*, so that no air can enter or leave the container. [This system may be a little difficult to

actually construct, perhaps, but it is not conceptually difficult!] Furthermore, the walls of the cylinder may be either *adiabatic* (i.e., not allowing any heat to flow through the wall) or *diathermal* (heat conductive) depending upon our particular needs. The external pressure acting on this system can be varied in a controlled fashion by adding to or removing from a pile of sand placed on top of the piston. Thus, this idealized system can interact *mechanically* with its surroundings and/or *thermally*. But, as long as the gas enclosed in the cylinder is a simple monatomic gas which cannot interact with the walls of the system, there will be no *chemical* processes which we will need to consider. This idealized system, composed of an *ideal* gas, is one of the simplest thermodynamic systems we can imagine, and we will make use of it extensively throughout our discussions.



**Fig. 1.1. An idealized system**

The Surroundings As mentioned above, a thermodynamic system (that part of the universe in which we are interested) is usually in contact with some other portion of the universe, the system's *surroundings* (or *environment*). In the case of a gas inside our idealized cylinder, the gas in the cylinder is the system, and the material of the walls of the cylinder and the piston compose the surroundings. One might, however, find it convenient to consider the entire cylinder with the contained gas as the system of interest, while the surroundings would be the air outside the cylinder. Likewise, the surroundings of the iceberg mentioned earlier must be the ocean water and the atmosphere. Thus, the *surroundings*, or *environment* of a system is that part of the universe which is *outside* the system of interest but which can in general interact with it. The surroundings of the system may be very complex and varied - as is the case where the iceberg interacts with both the ocean water and the atmosphere, or very simple - as in the case of a gas confined inside a container with adiabatic walls. In general, energy, either thermal or mechanical, and/or "mass" (i.e., microscopic particles) may be exchanged between the thermodynamic system of interest and the environment of that system. As mentioned earlier, we designate a system which can interchange mass as a **open** system, whereas one that cannot interchange mass is a **closed** system.



**Fig. 1.2 Two isolated gas systems which can interact with one another mechanically and/or thermally. The wall separating the two regions may be permeable, movable, adiabatic, or diathermal, or any combination of these.**

To keep our development of thermodynamics simple and easy to understand we will often consider *two* systems which are allowed to interact, and we will assume that these two systems are completely isolated from the rest of the universe (see Fig. 1.2). One of these systems (*A*) will be taken as the system of interest while the other system (*A'*) will act as the *environment* of the other system.

Types of Interactions between Systems. A system may interact with its surroundings in many different ways. We use certain terms to precisely describe the type of interaction which may be taking place between a system and its surrounding.

A system is said to be *isolated* if the system cannot interact with its surroundings *in any way* (i.e., if the system cannot gain or lose energy, particles, etc.). The universe as a whole may be considered as an isolated system. In fact, our solar system is very nearly isolated from the rest of our galaxy.

If there is no *material* interchange between the system and its surroundings, the system is said to be **closed**. But, even in a closed system, energy may still be exchanged between the system and its surroundings by thermal conduction through the adjoining wall or through the movement of the adjoining wall as the gas of the system expands or contracts. For a closed system, however, these processes must take place without a gain or loss of the particles which make up the system of interest. An **open** system, on the other hand, is one which may gain or lose material as it interacts with its surroundings. In practice, systems may be considered as open or closed depending upon whether a fixed *mass*, or a fixed *volume* is chosen for study. A **closed** system (also known as a **control mass**) consists of a *fixed amount of mass*, and no mass can cross its boundary. An **open** system (or **control volume**) is usually a properly selected region of space which may, for example, enclose a device that involves mass flow, such as a compressor, turbine, or nozzle. A simple example of an open system is a hot water heater. Suppose we want to know the amount of heat required to supply a steady stream of hot water at a given temperature. Since hot water leaves the water heater and is replaced by cold water entering the water heater, it is not convenient to concentrate of a fixed mass of water. Instead, we concentrate of the volume formed by the interior surface of the hot water heater. We will find that the applicable thermodynamic relationships differ, depending upon whether a system is open or closed. *It is, therefore, extremely important to properly recognize the type of system we have before we attempt to analyze it.*

A system may have a **mechanical** contact with its surroundings. For example, if the piston separating region *A* from region *A'* in Fig. 1.2 were to move to the right (increasing the volume of the gas in region *A*, but decreasing the volume of the gas in region *A'*) the expansion of system *A* is an obvious example of the case where the system is *doing mechanical work on its surroundings* (i.e., on system *A'*). Other forms of mechanical interaction are also possible. For example, a system may be composed of many charged particles arranged somewhat uniformly throughout the volume of the system. If an external electric field is present, the charges will respond to this field, and mechanical *work* will be done on the system which will store electrostatic energy in this system. Likewise, external magnetic forces, or gravity may cause the system to change its configuration in such a way as to store or release mechanical energy.

A system may interact **chemically** with its surroundings if the boundary separating the two systems will allow a chemical interaction to take place. A common example of this phenomenon is seen when a calcite rock (such as limestone) is slowly dissolved as water (which contains dissolved carbon dioxide) flows through cracks in the rock and over its surface to produce caves and caverns.

A system is said interact **thermally** with its surroundings when there is an energy change which takes place in the system without any change in the *macroscopic* properties of the system, such as the volume. For example in Fig. 1.2, assume that the wall between system *A* and *A'* would prevent any particle exchange or chemical interaction, and that the wall remains fixed. Any increase or decrease in the energy of system *A* must arise due to a *thermal* interaction. In this case the boundary between the system and its surroundings is said to be *diathermal* (i.e., the wall permits heat to pass through). Typically, a thermal interaction between two systems can be associated with an increase or a decrease in temperature of the two systems - the hotter system cooling off, and the cooler system warming up. However, as we shall see later on, *not all heat transfers result in a change in temperature.*

## THERMODYNAMIC EQUILIBRIUM

One of the most important concepts of thermodynamics is the concept of thermodynamic equilibrium. This concept arises from our everyday experience. If we place a cup of hot coffee on the counter and come back much later, we find that the temperature of the coffee has changed - it has cooled off. If we leave the coffee on the counter long enough, the temperature of the coffee becomes equal to the temperature of its surroundings. More precisely, if a system is *isolated* for a long period of time, the different properties of the system (the temperature

of our coffee; or the gas pressure, temperature, and volume for a ideal gas system) will eventually take on certain values *which will no longer change in time*. The *state* of the system at that point in time is *defined* to be a state of *thermodynamic equilibrium*. Once such a state is reached, the *state* properties or *macroscopic variables* will remain constant *unless and until the system is again allowed to interact with other parts of the universe*.

Thermal Equilibrium and Temperature. When we bring two systems together, we find that the hotter system will cool off, while the cooler system will heat up. This is according to experience, and is easily explained by saying that “heat” flows from the hotter system to the cooler system due to a thermal gradient, much like a fluid flows due to a pressure gradient or like electricity flows due to an electrostatic potential gradient. Since the flow of heat is often associated with a temperature change, we typically express the amount of heat which is added to or taken away from a system by the equation

$$\delta Q = C dT \quad (1.3)$$

where  $\delta Q$  is a differential amount of heat added to or removed from the system,  $dT$  is the differential change in temperature of the system, and  $C$  is the *heat capacity* of the system. By convention, we take  $\delta Q$  to be *positive* for heat added to the system. (Thus,  $\Delta Q = C(T_f - T_i)$  is positive if the final temperature of the system  $T_f$  is greater than the initial temperature of the system  $T_i$ .) The heat capacity  $C$  of a system is obviously proportional to the size of the system and to the composition of the system. And, although the heat capacity of a particular material is not the same in all temperature ranges, it is typically a slowly varying function of the temperature. Because the heat capacity as defined in this last equation depends upon the size of the system, we define the *specific* heat capacity, which is *independent* of the size of the system, by the relation

$$c = C/m, \quad (1.4)$$

giving

$$\delta Q = mc dT \quad (1.5)$$

Historically, the heat capacity of all substances was related to the heat capacity of water. The amount of heat required to heat 1 gram of water from 4 °C to 5 °C was *defined* to be 1 calorie, giving the specific heat capacity of water as 1 cal/g-°C in this temperature range.

Thus, when the temperature of the coffee in our coffee cup becomes equal to the temperature of the surroundings, we say that the coffee is in *thermal equilibrium* with its surroundings. The *temperature* of the cup of coffee is one of the macroscopic properties of our cup of coffee. We are all familiar with the general concept of temperature and we often make use of thermometers of various sorts (mercury thermometers, bimetallic coil thermometers, thermistors, thermocouples, etc.), but we need an *operational* definition of temperature. Just as we have precise definitions for the volume of a container or for the pressure exerted by a gas on the walls of that container, we must also have a precise definition for the *temperature* of the gas within the container.

The macroscopic parameter which we call *temperature* is, in fact, defined in terms of the concept of thermodynamic equilibrium. The temperature of a system is *that property of a system that determines whether it is in thermal equilibrium with other systems*. In order to understand this basic definition, consider again the definition of thermodynamic equilibrium. If two systems are connected by a diathermal wall (one which permits the transfer of heat), *and neither system changes*, we say that the two systems are in thermodynamic equilibrium with each other, and that these two systems have the same temperature. An extension of this idea is the so-called *zeroth law* of thermodynamics: *two objects in thermodynamic equilibrium with a third must be in thermodynamic equilibrium with each other*. This is a practical way of defining how one can measure temperature. One simply finds a device which has a measurable parameter (a thermometric property) such as length, resistance, color, etc. which changes with temperature. We can then use this “thermometer” to determine if two systems are at the same temperature. If they are, then the thermometric property of the thermometer will not change.

Just as there are a number of different devices which can be used to measure temperature, there are a number of different temperature scales which arise from using different *defined* temperatures and predetermined temperature intervals. For example, if we choose the melting point of ice and the boiling point of water as 0° and 100°, respectively, we have defined the Centigrade (or, more properly, the Celcius) temperature scale. If, on the other hand, we choose 32° and 212° for these two states, we have introduced the Fahrenheit temperature scale. Examples of temperature scales and the measurement of temperature are given in the problems.

**Mechanical Equilibrium.** A system is said to be in *mechanical equilibrium* when there is no change in energy of the system due to changes in *external properties* (or macroscopic properties). For example, a system may be in mechanical equilibrium if there is no change in the size or shape of the system due to changes in external pressure. In the idealized system shown in Fig. 1.1, the system would be in mechanical equilibrium as long as the volume of the gas did not change. (A dramatic example of a real system which is *not* in mechanical equilibrium is the example of exfoliated domes. These domes are produced as the great outward pressure from within the rock causes the rock to “pop” apart. These rocks were originally formed far beneath the surface as molten material cooled and solidified. The internal pressure had to be equal to the external pressure when the rock solidified. But when the rock was later exposed on the surface due to unloading by the erosion of the overburden, the internal pressure of the rock far exceeded the external pressure at the surface of the earth. Any weakness in the rock causes the rock to break apart.) Another example of a mechanical interaction is when a magnet is brought near a metal-oxide coating so that the orientation of the magnetic moment of the metallic material is changed (as in the storage medium of a hard disk drive).

**Chemical Equilibrium.** A third type of equilibrium is *chemical equilibrium*, where there is no change in the chemical nature of the system. For example, a mixture of  $H_2$  and  $O_2$  at the appropriate temperature will combine chemically to produce water vapor. Such a system is obviously not in chemical equilibrium. The chemical weathering of rocks is also a good example of a system (exposed rocks) which is not in chemical equilibrium.

### THERMODYNAMIC STATES, STATE VARIABLES, AND THE EQUATION OF STATE

**State Variables.** As was mentioned above, the *state* of an isolated system can be designated by giving the values of the system *parameters* or *variables* - those quantities which we can measure experimentally. The parameters or variables of interest are necessarily *macroscopic* quantities. (We cannot in general measure the specific microscopic conditions which may produce the observed macroscopic conditions. As we shall see in the study of statistical mechanics, for typical macroscopic systems there are a large number of very different microscopic situations which will yield identical values of the macroscopic quantities in which we are usually interested.) Some of the variables or parameters which might be of interest in a given system are the mass, pressure, volume, temperature, magnetic moment, dielectric constant, surface tension, etc.

**Intensive and Extensive Variables.** To make our development of thermodynamics as simple as possible we are first going to look at the simplest possible system. We will consider a gas in which the macroscopic parameters of interest are simply the pressure  $P$ , the mass  $m$  (or, alternately, the number of moles  $n$  or molecules  $N$  of the gas), the temperature  $T$ , and the volume  $V$ . If you think carefully about the four parameters which we just listed you will realize that the volume  $V$  of the system may be related in some way to the mass  $m$  of the system through the density of the gas. We quite often find that some of the parameters of a system depend upon the *size* of the system. Thus, if you take a system in thermodynamic equilibrium and subdivide it into smaller and smaller pieces, some of the measurable quantities, such as the total energy  $E$ , the mass  $m$ , the volume  $V$ , etc. are different for the smaller units than for the system as a whole [these depend upon the *extent*, or size, of the system]. Some parameters, however, are independent of the size of the smaller sub-units and have the same value in each of the individual units as in the larger system. Those parameters or variables of a system which *do not* depend upon the size of the system are called *intensive* variables, while those that *do* depend upon the size of the system are called *extensive* variables. An *extensive* variable, such as the volume  $V$  can be made *intensive* by dividing that variable by the mass (or the number of moles, or the number of atoms) of the system. Such a *reduced* variable is called the *specific* value of the parameter. For example, the *specific volume*,  $v$ , is given by

$$v = \frac{V}{m} \quad \text{or} \quad \frac{V}{n} \quad \text{or} \quad \frac{V}{N} \quad (1.6)$$

(Note that the specific volume of a gas is just the inverse of the density of the gas.) In this last equation, the volume  $V$  of the gas in a container is an *extensive* variable, and is expressed by a capital letter, while the *specific volume* is an *intensive* variable, and is expressed with small letters. This is the same process we utilized earlier in defining the *specific heat capacity*,  $c$ , by  $c = C/n$ , or  $C/m$ , where the heat capacity,  $C$ , is an extensive variable, and where  $n$  is the number of moles of a gas, and  $m$  is the mass of the substance. In most cases, extensive variables will be designated by upper-case letters, while intensive variables will be designated by lower case letters. Notable exceptions to this rule, however, are the *temperature* and *pressure* which are designated by capital letters, although they represent intensive variables.

**The Equation of State.** Intensive variables are typically local variables. That is, their particular value may change from point to point within the system of interest. For example, the density of a gas may vary

from point to point within a gas. This density gradient, however, will create a diffusive flow of gas from high density regions to low density regions until the density gradients are essentially eliminated. In the same fashion, there may be temperature or pressure gradients within the gas which will cause thermal and mechanical transport within the gas until these gradients are eliminated. *When the system is left undisturbed for long enough* (related to the relaxation time for the different processes within the system), *any gradients in the local parameters will eventually go to zero, and the system is said to be in a state of thermodynamic equilibrium*. In such a state, the macroscopic properties of the system, such as pressure and temperature, have specific values *which are the same at all points within the system*. The values of the macroscopic parameters of a system in a state of thermodynamic equilibrium are determined by the particular state (or condition) of the system and are called *state variables*. Thus, when the system is in a particular thermodynamic state, a specific value of all state variables is uniquely defined. This means we can write a relationship between the parameters of the system of the form

$$f(P, T, v) = 0$$

This equation implies that there is some specific relationship between the parameters of the system when that system is in a specific equilibrium state. Likewise, a knowledge of the specific value of all the state variables uniquely defines a particular thermodynamic state of the system.

The number of variables required to completely specify the state of the system depends on the particular system involved. If the system is a gas with a definite number of similar molecules at moderate temperatures and pressures, the only parameters required to specify the state of the system are the pressure  $P$ , the volume  $V$ , the temperature  $T$ , and the number of molecules  $N$  or moles  $n$  of the gas (a *gram-mole* is defined as the number of molecules of gas which have a mass in grams equivalent to the molecule's molecular weight and is given by  $6.0225 \times 10^{23}$  particles). As we mentioned above, the volume  $V$  of the system is an *extensive* variable. In many thermodynamics texts the equations are expressed in terms of the *specific volume*,  $v$ , so that the equations which are developed will not depend upon the size of the system. This also reduces the number of macroscopic parameters needed to completely specify the state of the system. Thus we might say that the parameters for our ideal system are the *specific volume*  $v$ , the pressure  $P$ , and the temperature  $T$  of the system, giving us only three distinct intensive variables which can be used to completely characterize the system, i.e.,

$$f(n, P, V, T) = f(P, v, T) = 0 \quad (1.7)$$

This equation expresses the fact that the temperature is a function of the pressure and the (specific) volume; that the pressure is a function of the temperature and the specific volume; or that the specific volume is a function of the temperature and pressure, as expressed explicitly by the following equations:

$$\begin{aligned} T &= T(v, P) \\ P &= P(v, T) \\ v &= v(P, T) \end{aligned} \quad (1.8)$$

These three equations indicate that *the thermodynamic state of this simple gas is completely specified by two independent, intensive properties* - and we are at liberty to pick any two.

Although we are confident that such relationships exist between the observed properties of our gas, we do not often know in advance what these specific formulae are. Nature, on the other hand, knows quite well how the pressure is related to the temperature and the specific volume of a particular substance. *One of the objectives of thermodynamics is to determine by experimental methods what the equation of state of different substances might be, so that we can understand and predict how one parameter might vary as we change another one.*

These thermodynamic parameters have well defined values *only for a thermodynamic state in equilibrium*. If a system is suddenly brought into contact with another system at very different temperature, there will be thermal gradients set up inside the system and the temperature will *not* be uniform throughout the system. (There may also be pressure differentials, shock waves, turbulence, etc., established in the system.) By making measurements of systems in equilibrium, however, we can determine the equilibrium values of the parameters of a system and, perhaps, determine a mathematical expression for the relationship among those variables.

### THERMODYNAMIC PROCESSES FOR PURE SUBSTANCES

A substance with a fixed chemical composition throughout is called a *pure* substance. A pure substance, however, does not have to be a single chemical compound. For example, air contained within a fixed volume at normal temperature and pressure is considered a pure substance since the composition of air is the same at all

parts of the system. If the temperature of this system were to be decreased to the point where some of the components of air began to condense, however, this would no longer be a pure substance. Likewise, a mixture of oil and water would not be a pure substance since the oil and water do not mix.

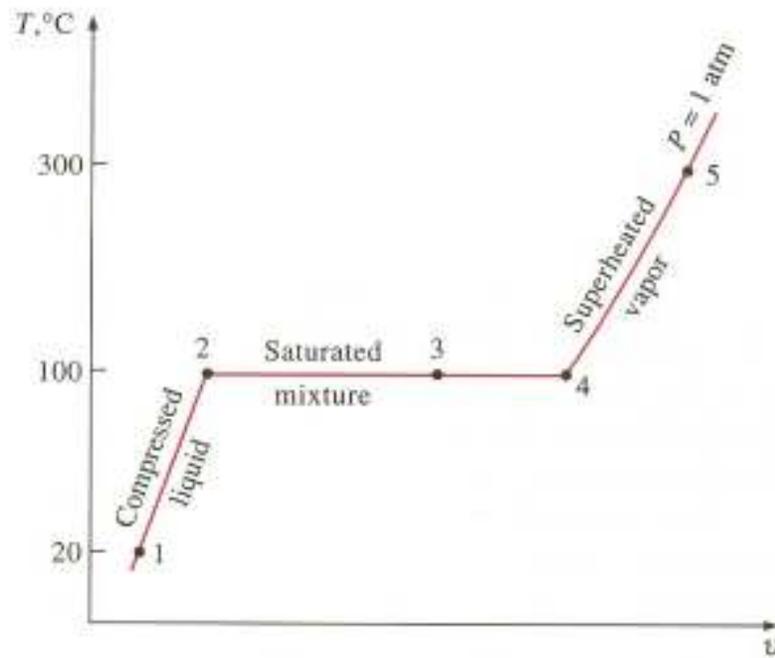
Practically all pure substances can exist in different phases depending upon the temperature and pressure. The most common example, water, can exist as a gas, a liquid, and a solid within the temperature and pressure ranges present on the surface of the earth. In the gaseous phase the molecules can move about freely within a fixed volume, bouncing off each other and the walls of the container, and completely filling the volume. In the liquid phase, the molecules are loosely attracted to each other and form groups of molecules that have a more or less fixed volume and density, but which can still move about when subjected to external shear forces. In a closed container the liquid and gaseous phase are typically in equilibrium. In the solid phase the molecules are more or less fixed in place, but may oscillate about their equilibrium position. However, many solids exist in one of several different phases. Each phase is characterized by a specific molecular arrangement which is homogeneous within a given phase. Different phases may actually coexist within the solid and can be identified by an easily identifiable boundary surface. For example, water ice may exist in *seven* different phases at high pressures.

Phase-Change Processes for Pure Substances. If we add heat energy to a pure substance, the temperature of that substance will rise until a critical point is reached where additional heat energy will begin to cause the inter-molecular bonds to break. As an example, consider an amount of water at 1 atm and 20°C contained in a closed cylinder. We assume the cylinder is capped by an ideal (massless, frictionless, tight-fitting) piston which rests on top of the water. The water in this phase is called a *compressed*, or *subcooled liquid* (meaning that it is not about to evaporate). If we now add heat to the system, the water will expand slightly as the temperature rises, increasing its specific volume (process 1→2 of Fig. 1.3). The pressure of the liquid will still remain constant at 1 atmosphere as the piston moves upward. This process will continue until the temperature of the water reaches 100°C (point 2). Once the water reaches 100°C any addition of heat will cause the intermolecular bonds to break and the water will begin to vaporize. A liquid which is about to vaporize is called a *saturated liquid*. As additional heat is added to the system the amount of saturated water will begin to decrease and the amount of water vapor will begin to increase, but the temperature of the mixture will remain constant at 100°C. This process (2→3) will continue as heat is added to the system until all the water is changed into vapor. At each point along the constant temperature curve the liquid and vapor coexist in equilibrium as a *saturated liquid-vapor mixture*. Along this curve any addition of heat energy increases the amount of water vapor and decreases the amount of liquid water, while any loss of heat energy decreases the amount of water vapor and increases the amount of liquid water.

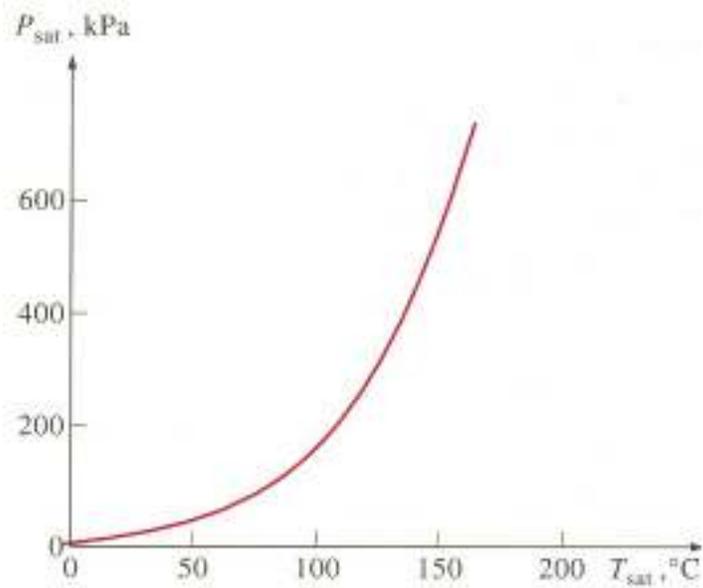
Once the phase-change process is completed we again have a single-phase substance (in this case water vapor), and the temperature of the vapor will begin to rise as we add additional heat (process 4→5). The water vapor in this last process (which is no longer at the point of condensation) is called a *superheated vapor*.

The processes we have described are reversible. If we begin with the superheated vapor and slowly remove heat from the system, the thermodynamic states will be retraced, provided we maintain the same, constant external pressure.

Saturation Temperature and Pressure. If we increase the pressure on our sample of water, we find that the we can raise the temperature beyond 100°C before the water begins to vaporize (or boil). In fact, we find that the temperature at which water begins to boil increases with pressure. At a given pressure, the *temperature* at which the liquid begins to boil is called the *saturation temperature*. Likewise, the *pressure* at which a liquid boils for a given temperature is called the *saturation pressure*. If we plot the saturation pressure vs. the saturation temperature, we obtain a *liquid-vapor saturation curve* such as that shown in Fig. 1.4 on the next page. Obviously, the  $T$  vs.  $v$  plot for water as it passes through a phase change must be modified if we change the pressure exerted on the water. To accomplish this, we can think of adding masses to the piston which sits on top of the water. Just as before, we can plot the temperature of the water vs. the intensive volume as heat is added to the system. For each different external pressure, we will see a curve similar to the one we have in Fig. 1.3 except for the fact that the saturation temperature increases and the width of the saturated liquid-vapor region (the saturation line) grows narrower with increasing pressure as shown in Fig. 1.5. The width of the saturation line continues to grow narrower as the pressure increases until it disappears altogether. This occurs at the *critical point*, defined by a critical temperature, specific volume, and pressure, and is the point where the saturated liquid and vapor states are identical. At this point it is impossible to visually detect a liquid surface. Above the critical pressure there is no distinct phase-change process. The intensive volume increases continuously with increasing temperature and we can never tell when we pass from the condensed liquid to the superheated vapor.



**Fig 1.3.**  $T$ - $v$  diagram of the heating process of water at constant pressure. {from Cengel and Boles}



**Fig 1.4.** The liquid-vapor saturation curve of a pure substance (numerical values are for water). {from Cengel and Boles}

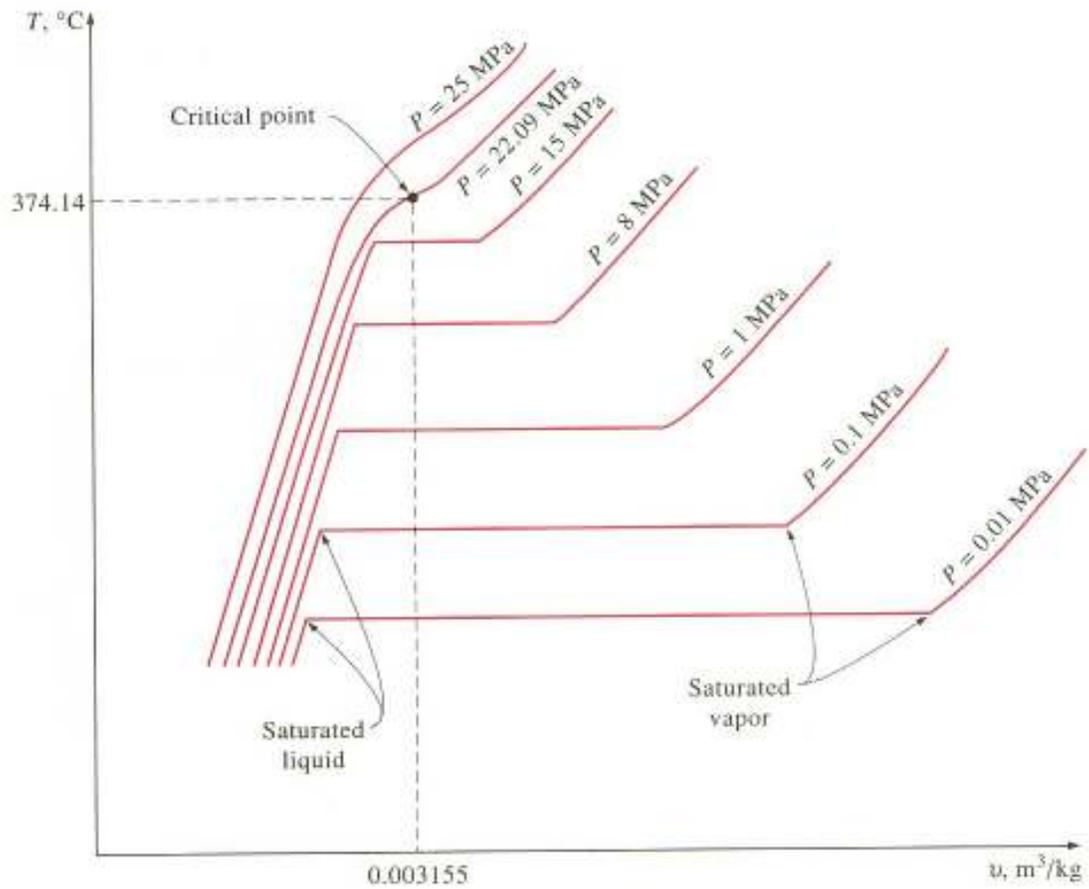


Fig. 1.5.  $T-v$  diagram of constant-pressure phase-change processes of a pure substance at various pressures (numerical values are for water). {from Cengel and Boles}

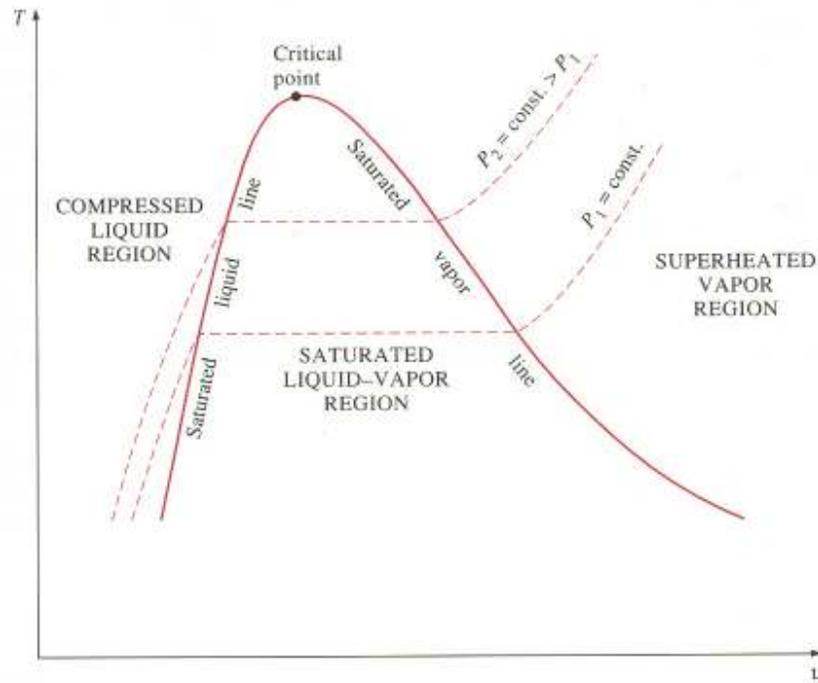


Fig. 1.6.  $T$ - $v$  diagram for a pure substance. {from Cengel and Boles}

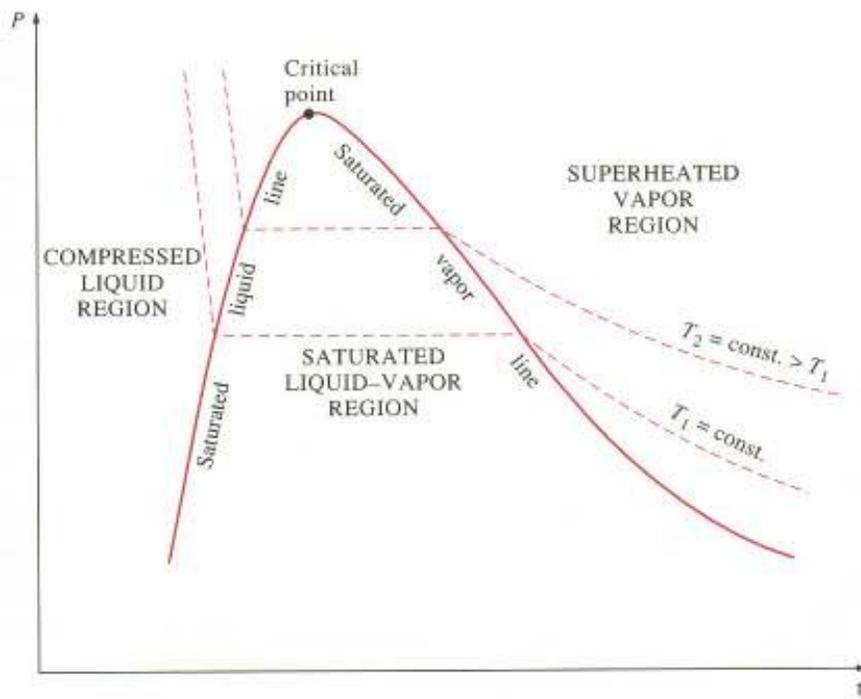


Fig. 1.7.  $P$ - $v$  diagram for a pure substance. {from Cengel and Boles}

These same phase-change processes can also be plotted on a  $P$  vs.  $v$  diagram. However, the *constant temperature* lines on the  $P$  vs.  $v$  graph have a downward trend, while the *constant pressure* lines on the  $T$  vs.  $v$  graph have an upward trend. This can be seen in Figs. 1.6 and 1.7.

Three-Dimensional Representation of Process Diagrams Extended to Include the Solid Phase. The diagrams in Figures 1.8 and 1.9 represent three-dimensional  $P, v, T$  surfaces which include the solid phase. Figure 1.8 represents a substance which contracts upon freezing, while Figure 1.9 represents a substance which expands upon freezing (like water). If each three-dimensional surface is projected onto the  $P$ - $T$  and the  $P$ - $v$  planes, respectively, we obtain the two-dimensional process diagrams shown in Fig. 1.8 (a) and (b) and in Fig. 1.9 (a) and (b). For each type of material, you will see a region on the  $P, v, T$  surface where the liquid and vapor phases can co-exist as well as a region where the solid and vapor phases can co-exist. These two regions are separated by the *triple line*. Along this line the substance can exist with all three phases in equilibrium. On a  $P$  vs.  $T$  graph (see the detailed drawing of Fig. 1.10), often called the *phase diagram*, this triple line appears as a *triple point!* On this graph, all three phases of a substance are separated from each other by three lines, the sublimation line, the vaporization line, and the melting line which all intersect at the triple point.

The three-dimensional  $P, v, T$  surfaces shown in Fig. 1.8 and 1.9 represent *all possible states of thermodynamic equilibrium* for that particular substance. This means that we can represent any *quasi-static process* (one which occurs slowly enough that the system is always essentially in equilibrium) for this substance by a line on this  $P, v, T$  surface. It would be nice to have a simple mathematical equation which would relate the various properties of any real substance (i.e., it would be nice to have a simple mathematical formula which would represent all the points of the  $P, v, T$  surface). Unfortunately, such a simple relationship, valid for all values of the properties of the system, does not generally exist. As a result, we often make use of tables of data which give relationships between the system properties and the critical temperature, pressure, and volumes, along with the saturation temperatures and pressures for various substances. These can be found for some substances in the Appendix. For many *gases* at low pressures, however, there *is* a simple mathematical relationship between the observable properties of the gas, known as the *ideal gas law*.

### THE EQUATION OF STATE FOR AN IDEAL GAS

Robert Boyle showed empirically that the pressure of a gas is inversely proportional to the volume of the gas when the gas is held at constant temperature, or

$$PV = \text{constant} \quad (= \text{a function only of the amount of gas present}) \quad (1.9)$$

Now for *different amounts* of the same gas, the constant of proportionality is different, but if the *specific* volume is used, we find that

$$\frac{PV}{n} = Pv = K \quad (1.10)$$

where  $K$  is a function *only* of the temperature and not of the size of the system (or number of molecules).

In later experiments Charles demonstrated that the product of the pressure and the specific volume, when plotted against the temperature, resulted in an approximate straight line for the case where the pressure was relatively low. The value of  $PV/n$  for this straight line was found to be  $2.271 \times 10^3$  Joules per mole at the triple point of water ( $0^\circ\text{C}$ ), and  $3.102 \times 10^3$  Joules per mole at the boiling point of water ( $100^\circ\text{C}$ ) for almost all gases at relatively low pressure. If we assume that this is a good approximation for *all* gases, then we can write the equation for this *ideal* gas as

$$\frac{PV}{n} = a + RT \quad (1.11)$$

where  $a$  and  $R$  are constants and where  $T$  is the temperature defined according to our chosen scale (the so-called Celsius scale). If we plug in the values of  $PV/n$  mentioned above and solve for  $a$  and  $R$  we obtain:

$$a = 2.271 \times 10^3 \text{ Joules/mole} \quad \text{and} \quad R = 8.314 \text{ Joules/mole-}^\circ\text{C}.$$

From our equation for  $PV/n$  we can therefore write:

$$PV = n(a + RT) \quad (1.12)$$

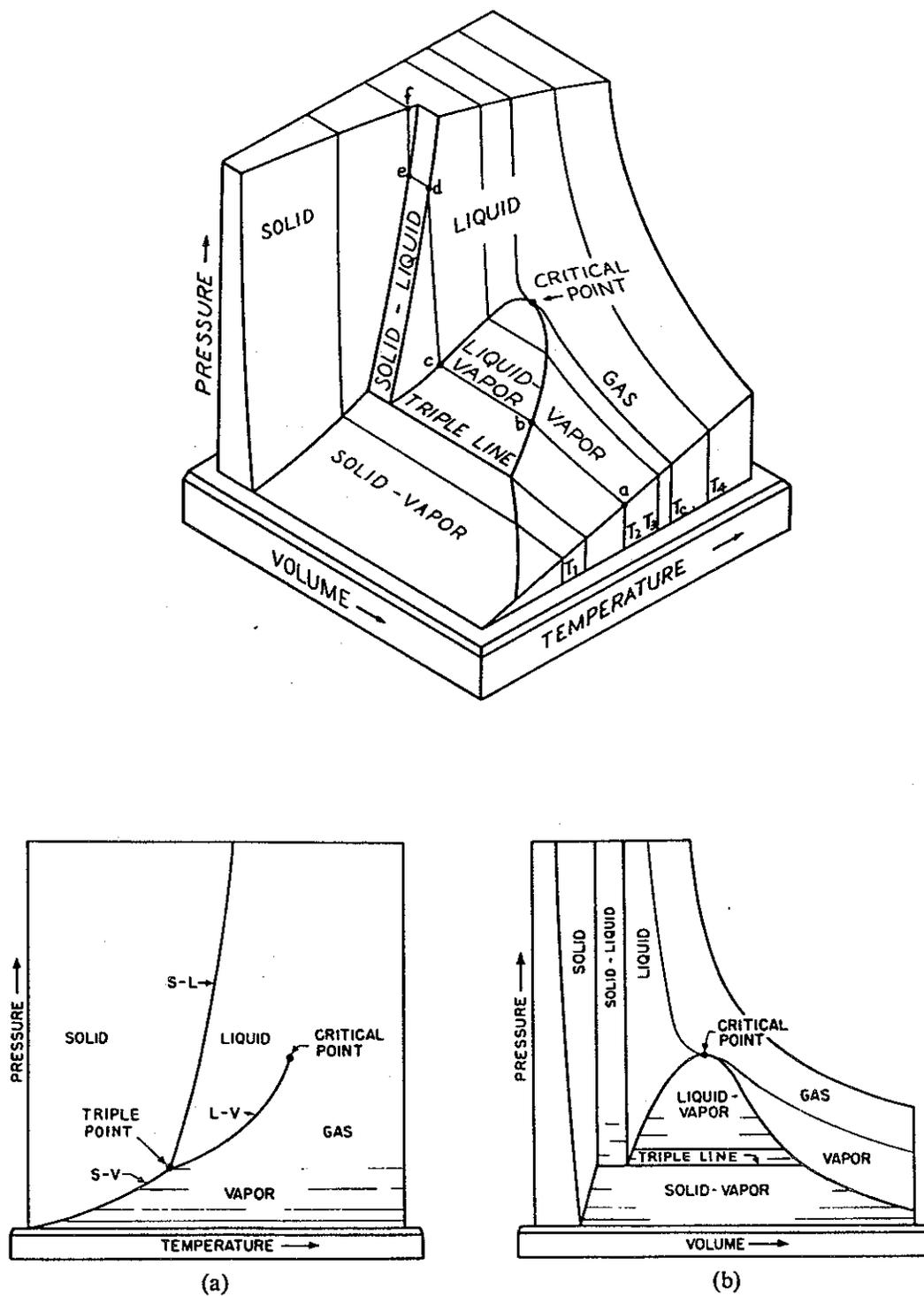


Fig. 1.8. The  $P$ - $v$ - $T$  surface for a substance that contracts upon freezing and the projection of this surface onto (a) the  $P$ - $T$  plane, and (b) the  $P$ - $v$  plane.

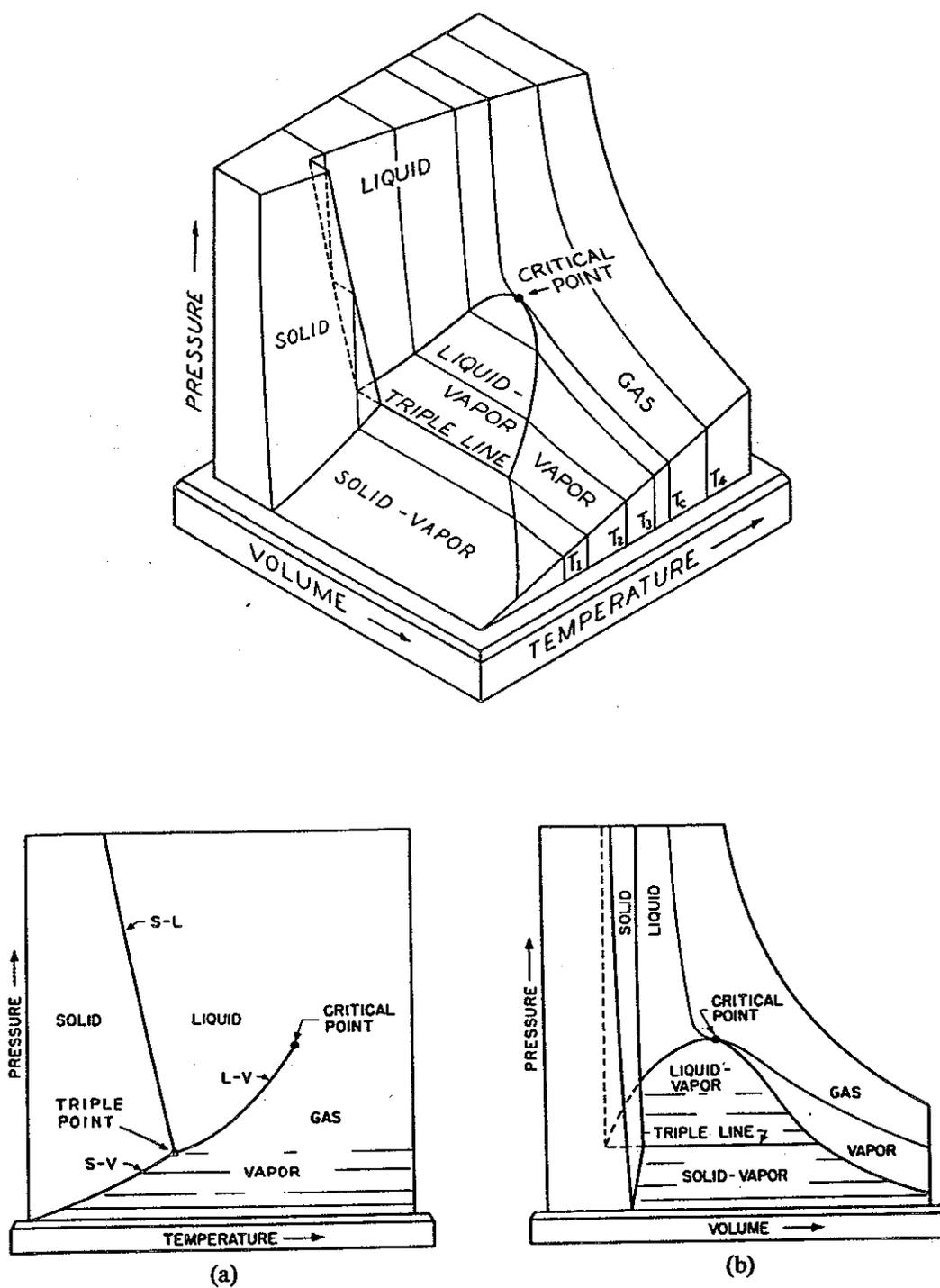
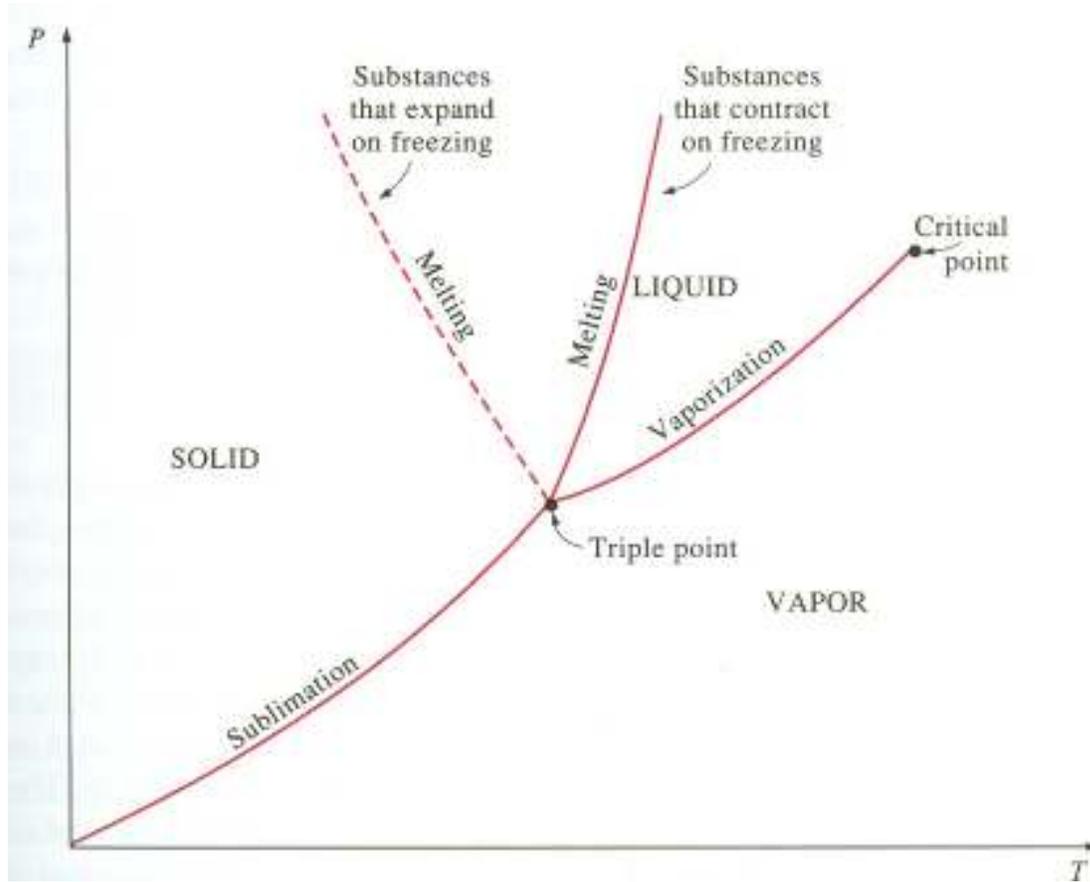


Fig. 1.9. The  $P-v-T$  surface for a substance that expands upon freezing (like water) and the projection of this surface onto (a) the  $P-T$  plane, and (b) the  $P-v$  plane.



**Fig. 1.10.** The  $P$ - $T$  or *phase diagram* for a pure substance. {from Cengel and Boles}

or

$$PV = na + nRT \quad (1.13)$$

or, finally,

$$PV = nR(T_0 + T) = nRT \quad (1.14)$$

where  $T_0 = a/R = 273.2 \text{ }^\circ\text{C}$ . This last equation defines a new temperature scale which we call the thermodynamic or Kelvin scale with

$$T[\text{K}] = T_0[^\circ\text{C}] + T[^\circ\text{C}] = 273.2 \text{ }^\circ\text{C} + T[^\circ\text{C}]. \quad (1.15)$$

(The proper units for each quantity are indicated in the brackets. The present convention is for there to be a degree symbol associated with the Celsius temperature scale, but not with the Kelvin scale.)

The equation of state for an *ideal gas* is, therefore,

$$PV = nRT \quad (1.16)$$

where  $P$  is the pressure,  $V$  is the *extensive* volume,  $n$  is the number of moles of the gas,  $R$  is a universal constant called the *ideal gas constant*, and  $T$  is the temperature in Kelvin. In physics we often find it more convenient to specify the number of particles  $N$  rather than the number of moles  $n$  and write the *ideal gas law* as

$$PV = NkT \quad (1.17)$$

In this equation we introduce a new constant  $k$  which is known as the Boltzmann constant. This constant is related to the ideal gas constant  $R$  by the relation

$$nR = Nk \Rightarrow k = \frac{nR}{N} \quad (1.18)$$

We can find the value of  $k$  (Boltzmann's constant) by setting  $n = 1$  and  $N = N_A$  (where  $N_A$  is Avogadro's number –  $6.0225 \times 10^{23}$  molecules/gram-mole). We obtain:

$$k = 1.38 \times 10^{-23} \text{ Joules/molecule-K} \quad (1.19)$$

In terms of *intensive variables* we can write the ideal gas law as

$$Pv = kT \quad \text{or} \quad Pv = RT \quad (1.20)$$

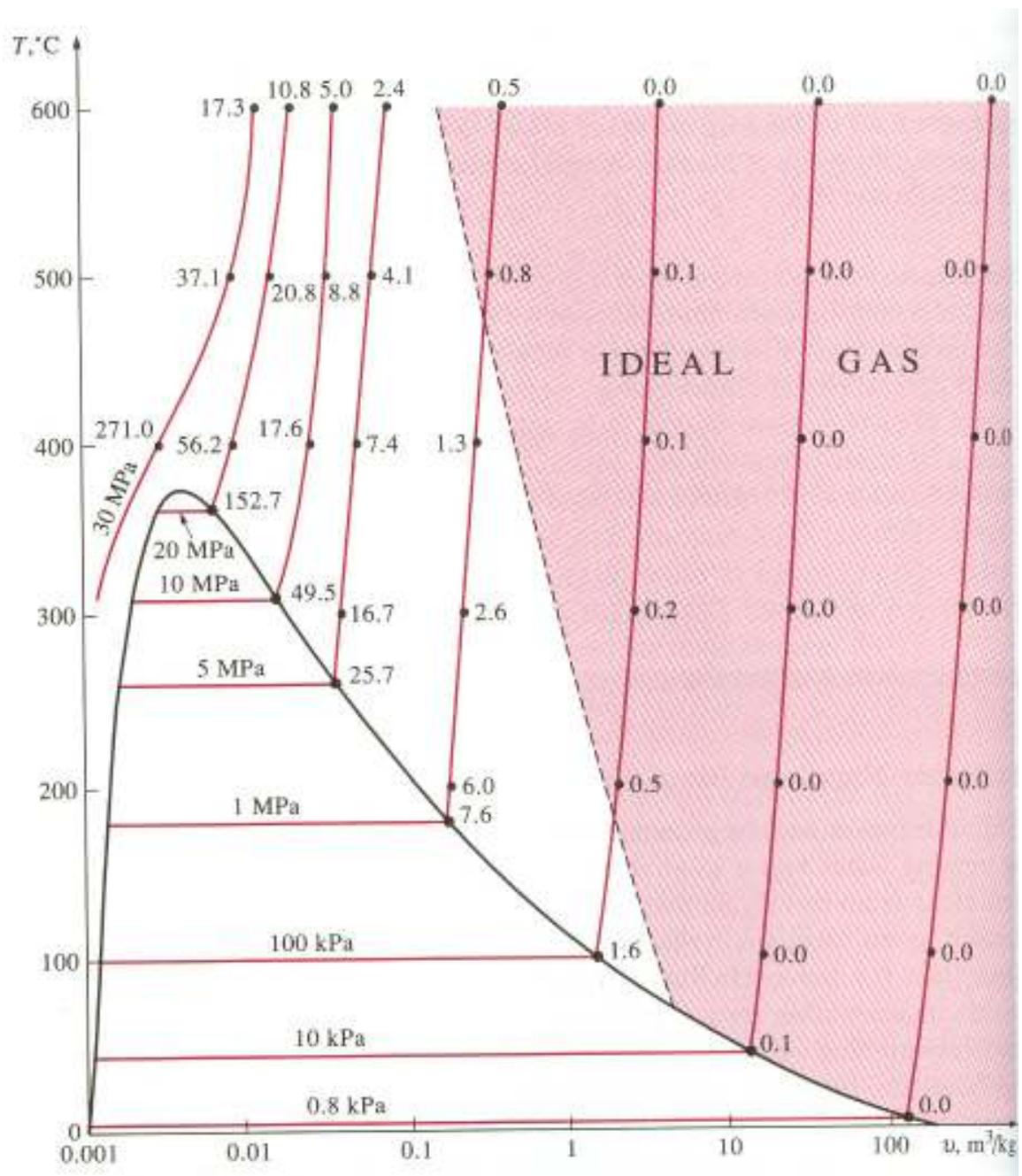
where  $v = V/N$ , or  $v = V/n$ , respectively. (The left side of the equations above,  $Pv$ , has units of energy per mole or energy per molecule. You should recall from modern physics that Boltzmann's constant is in terms of energy in Joules (or eV) per molecule per Kelvin, which means that the universal gas constant must be in terms of the energy in Joules (or eV) per mole per Kelvin.)

Based upon some fairly simple experiments, we have determined an equation of state which gives a functional relationship between the pressure, the specific volume, and the temperature of a gas at low pressures. But what do we mean by *low* pressures? Different substances are gases at different temperatures and pressures! For example, under “normal” conditions on the earth's surface, carbon dioxide is a gas, but at the low temperatures found on Mars, carbon dioxide often “freezes out” and solidifies into what we call dry ice. (It is called “dry” ice because at normal atmospheric pressure on the surface of the earth solid carbon dioxide will not *melt*; carbon dioxide simply changes phase from a solid to a gas. This same phenomenon would also occur for water at pressures *below* the triple point pressure of 0.61 kPa.)

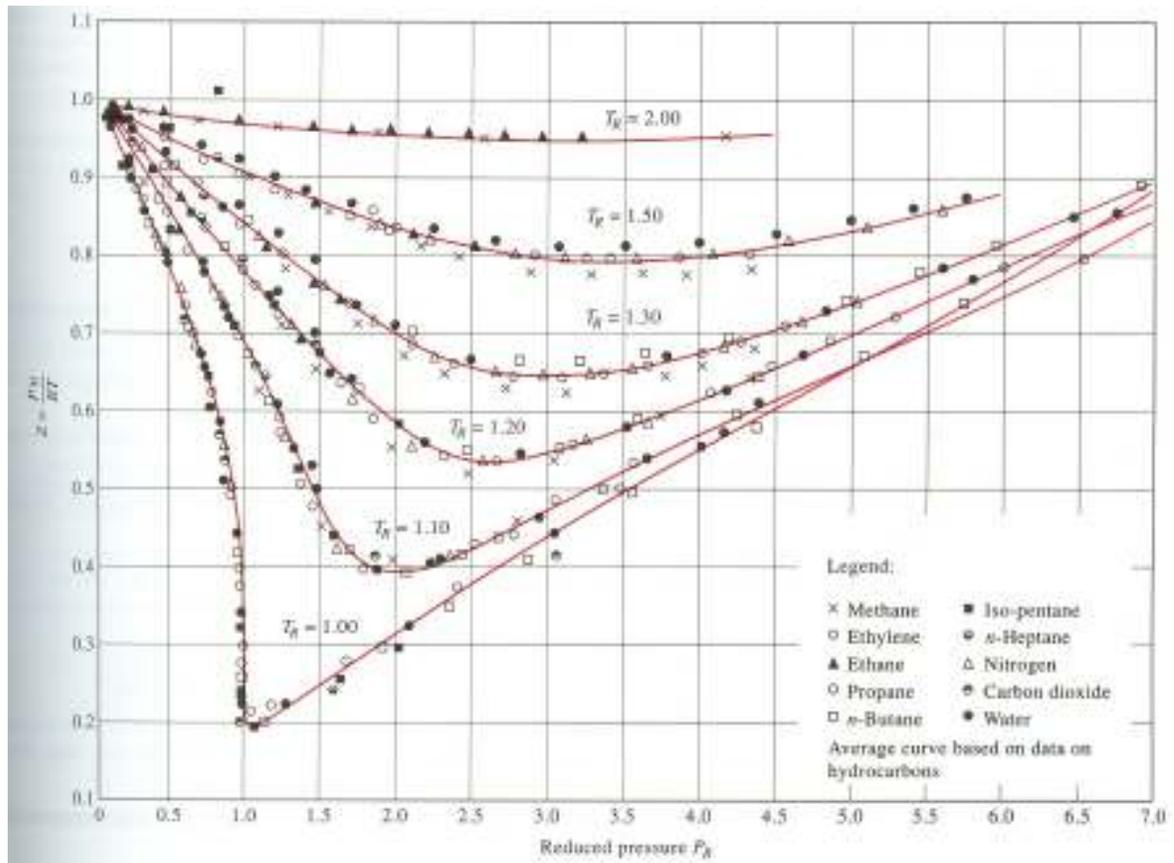
To determine just how well real gasses can be characterized by the ideal gas equation, we introduce the *compressibility factor*,  $Z$ , defined by

$$Z = \frac{Pv}{RT} = \frac{v}{RT/P} = \frac{v_{actual}}{v_{ideal}} \quad (1.21)$$

where  $Z$  will be equal to unity for the case of an ideal gas.



**Fig. 1.11.** Percentage error involved in assuming steam to be an ideal gas, showing the region in which steam can be treated as an ideal gas with less than 1% error. [The percentage error is calculated using the equation  $100\% \times |v_{\text{table}} - v_{\text{ideal}}|/v_{\text{table}}$ .] {from Cengel and Boles}



**Fig. 1.12.** A comparison of the compressibility factor for various gases as a function of reduced parameters. {from Cengel and Boles}

This compressibility factor is typically less than unity for real gasses. This is reasonable since the model for an ideal gas neglects the actual intermolecular attraction experienced by any real gas, and this intermolecular attraction would tend to effectively reduce the specific volume. The compressibility factor becomes *much less* than unity when the real gas is near its critical temperature and pressure.

Under normal conditions, most familiar gases like air and its lighter constituents (oxygen, nitrogen, hydrogen, etc.) give errors of less than one percent when treated as ideal gases. Heavier gases, however, tend to deviate somewhat from the ideal gas equation. As an example, Fig. 1.11 shows a  $T$ - $v$  plot for water vapor showing the percentage error involved in making the ideal gas approximation. The region where this error is less than 1% is designated as the ideal gas region. Thus, different gases may behave quite differently at the same temperature and pressure, one acting more like an ideal gas than the other. We find, however, that all gases behave very much the same at temperatures and pressures normalized relative to their critical temperature and pressure. (Remember that the critical point of a substance is that temperature and pressure where the saturated vapor and saturated liquid coexist.) If we define the reduced temperature and pressure by the equations

$$T_R = T/T_{cr} \quad \text{and} \quad P_R = P/P_{cr}$$

we find that a plot of the compressibility factor as a function of these reduced quantities is essentially independent of the particular gas as shown in Fig. 1.12. From this figure we see that the ideal gas law works well (i.e.,  $Z \approx 1$ ) for any real gas: 1) for very low pressures ( $P_R \ll 1$ ) regardless of the temperature, and 2) at high temperatures ( $T_R > 2$ ) regardless of the pressure. The greatest deviation from the ideal gas law occurs near the critical point (where  $P_R$  and/or  $T_R = 1$ ).

Although the ideal gas law is somewhat limited in its application to real gases, we find it useful to postulate the existence of an *ideal gas* which obeys the ideal gas law *for all pressures, and temperatures*. This is true primarily because of the simple relationships between the properties of an ideal gas. We must remember, however, that the ideal gas law is just an approximation to reality.

### A BETTER APPROXIMATION TO REAL GASES THE EQUATION OF STATE FOR A VAN DER WAAL GAS

In the last section, it was argued that the equation of state for an ideal gas is a good approximation for real gases as long as we are dealing with relatively low reduced pressures. However, as the pressure of a gas is increased at constant temperature, the average distance between molecules decreases and intermolecular forces become more important. The equation of state for an ideal gas, however, implies that the specific volume of the gas would continue to decrease as the pressure increases (refer to the  $P$ - $v$ - $T$  surface shown in Fig 1.13).

But even if the molecules could be modeled as hard spheres (i.e., there is no interaction between molecules beyond the radius of a molecule), the volume could not decrease beyond a certain limit. Thus, if we considered each molecule to have a volume  $\frac{4}{3}\pi a^3$ , where  $a$  is the radius of the molecule, then the volume of the gas could never become less than  $N$  times this volume.

Using this argument, we let the *specific volume* occupied by the molecules themselves be given by

$$b = \frac{V_{mol}}{n} = \frac{N \times \frac{4}{3}\pi a^3}{n} \quad (1.22)$$

which leads to a more accurate equation of state represented by the equation

$$P(v - b) = RT \quad (1.23)$$

In this equation the size of the individual molecules is taken into account, and  $(v - b)$  represents the total specific volume accessible to all the molecules of the system (the volume of the container less the volume occupied by all the other molecules).

In addition to this correction, we know that in most circumstances there really is an attraction between the molecules that make up a gas. This attraction is typically relatively weak (the induced dipole-dipole interaction being a  $1/r^6$  force). A correction for this attraction can be incorporated by considering the pressure that the gas exerts on the wall of its container. When a molecule is completely surrounded by other molecules any attraction between the particles would average out to zero. As a single molecule approaches the wall, however, there are more molecules on one side of this molecule (the side away from the wall) than there are on the other side of this molecule (the side toward the wall). This means that there is a net force on the molecule *away from the wall*. This net force effectively *reduces* the pressure which the gas would exert on the wall of the container. Thus, the

pressure exerted on the walls of the container is actually *less* than the pressure would be if there were no intermolecular forces. This leads to the equation

$$P = \frac{RT}{(v-b)} - \delta P \quad (1.24)$$

where  $P$  is the actual pressure on the wall,  $RT/(v-b)$  is the pressure that would be exerted by the molecules on the wall if there were no interactions, and  $\delta P$  is the reduction in pressure due to molecular attraction. Now if we assume the interaction between molecules arises due to induced electric dipole moments, the electric force between these dipoles is of the order  $1/r^6$  or  $1/v^2$ . Thus, we expect the change in pressure to be proportional to the inverse square of the specific volume. This means that the last equation can be written as

$$P = \frac{RT}{(v-b)} - \frac{a}{v^2} \quad (1.25)$$

or

$$\left(P + \frac{a}{v^2}\right)(v-b) = RT \quad (1.26)$$

This form of the equation of state for a gas was first proposed by Van der Waal. In terms of *extensive* variables this equation can be written

$$(P + an^2/V^2)(V - nb) = nRT, \quad (1.27)$$

which is somewhat more difficult to remember.

A diagram of the  $P, v, T$  surface for a Van der Waal gas is shown in Fig. 1.14. As you can see, this surface is somewhat different from the  $P, v, T$  surface for an ideal gas. When the  $P, v, T$  surface is projected onto the  $P-v$  plane we see that there can be three different values of the pressure (for example, a, b, and c on the diagram) which satisfy the Van der Waal equation for any temperature below the critical temperature  $T_c$ . This type behavior is what we expect from a substance which changes phase and does resemble the  $P, v, T$  diagrams shown earlier for real substances.

Van der Waal's equation should reduce to the ideal gas equation as the specific volume becomes large. To show this, we expand the equation in inverse powers of the specific volume:

$$P = \frac{RT}{v(1-b/v)} - \frac{a}{v^2} = \frac{RT}{v}(1-b/v)^{-1} - \frac{a}{v^2} \quad (1.28)$$

or

$$P = \frac{RT}{v} \left(1 + \frac{b}{v} + \left(\frac{b}{v}\right)^2 + \dots\right) - \frac{a}{v^2} \quad (1.29)$$

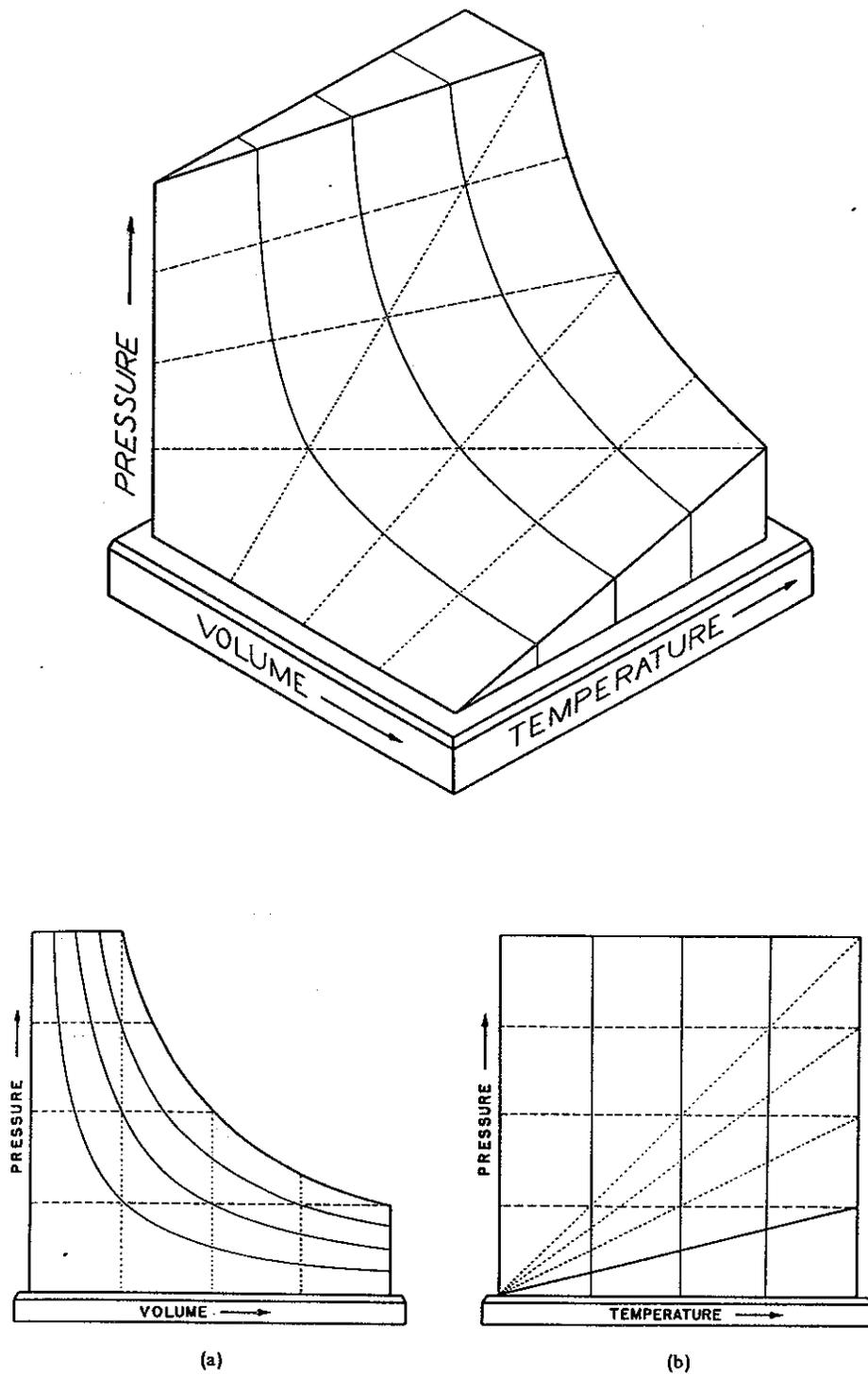
which can be written in the form

$$P = \frac{RT}{v^1} + \frac{RTb-a}{v^2} + \frac{RTb^2}{v^3} + \dots \quad (1.30)$$

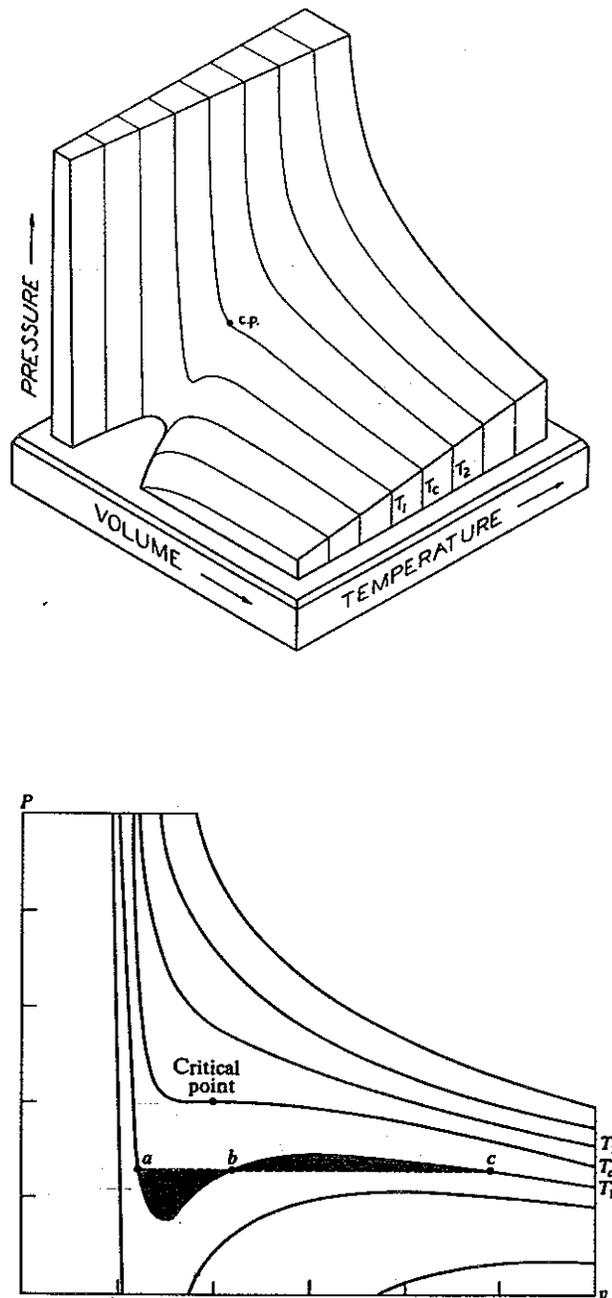
This last equation is in the form of a *virial expansion* of the equation of state. A virial expansion has the form

$$P = \sum_i \frac{C_i}{v^i} \quad (1.31)$$

where the  $C_i$ 's are the *virial coefficients*, and are typically functions of the temperature. The virial expansion often serves as a very good approximation to real gases, where the  $C_i$ 's are chosen to give the best fit to the data. Obviously, as the specific volume of the system increases the first term is the most dominant, and, the virial expansion simply reduces to the ideal gas law.



**Fig. 1.13.** The  $P-v-T$  surface for an ideal gas, and its projection onto the  $P-v$  and  $P-T$  plane.



**Fig. 1.14.** The  $P-v-T$  surface for a Van der Waal's gas, and the projection of this surface onto the  $P-v$  plane. The region where three different values of the intensive volume give the same pressure is probably related to a phase-change region.

### EQUATIONS OF STATE FOR OTHER SYSTEMS

Corresponding equations of state may be determined for liquids and solids. A simple one, valid for many solids at moderate temperatures and pressures is given by

$$V = V_0 (1 + \beta T - \kappa P), \quad (1.32)$$

where  $\beta$  is the thermal coefficient of expansion and  $\kappa$  is the isothermal compressibility, respectively defined by the relations:

$$\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad \kappa = - \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T. \quad (1.33)$$

For solids, both  $\beta$  and  $\kappa$  are small quantities ( $\beta \approx 10^{-6}$ ;  $\kappa \approx 10^{-12}$ ) but they are not quite constant, varying slightly with temperature and pressure (see Fig. 1.15 and 1.16 on the next page).

Similarly, we might be interested in the magnetic moment of a paramagnetic salt, and how this varies with the temperature (or volume, or pressure). A very good approximation for the magnetic moment of a paramagnetic salt valid for small fields and relatively low temperatures is given by the Curie law:

$$\mathcal{M} = \mathcal{D} \frac{\mathcal{H}}{T} \quad (1.34)$$

where  $\mathcal{M}$  is the magnetic moment of the salt,  $\mathcal{D}$  is the Curie constant,  $\mathcal{H}$  is the magnetic field, and  $T$  is the temperature. For such a salt, variations in pressure and volume are usually negligible.

### RELATIONSHIPS BETWEEN SYSTEM PARAMETERS AND PARTIAL DERIVATIVES

We have pointed out that the equation of state for both the ideal gas and for the Van der Waal gas can be represented by a three-dimensional surface upon which are located all the possible equilibrium states of the system in question. For a real system we may or may not know exactly what that surface is like (i.e., we may or may not know a correct mathematical expression which will properly describe *all* the equilibrium states of the system). But we may be able, even in the case where we do not know the equation of state exactly, to determine the characteristics of the  $P, v, T$  surface (i.e., to determine the equation of state) in some region around a particular set of values  $P_0, v_0, T_0$ . We can do this by determining the slope of the mathematical surface in the region around  $P_0, v_0, T_0$ , i.e. by determining the rate of change of one of the variables with respect to the other two in this region. For example, the differential change in the *state variable*  $P$ , as a function of differential changes in  $v$  and  $T$  can be expressed in the following way:

$$dP = \left( \frac{\partial P}{\partial v} \right)_T dv + \left( \frac{\partial P}{\partial T} \right)_v dT \quad (1.35)$$

where the expression,  $\left( \frac{\partial P}{\partial v} \right)_T$  is the partial derivative of pressure with respect to volume with the temperature held constant. Likewise, we can write the change in temperature of the system in terms of changes in the volume and the pressure

$$dT = \left( \frac{\partial T}{\partial v} \right)_P dv + \left( \frac{\partial T}{\partial P} \right)_v dP, \quad (1.36)$$

and we can write the change in specific volume of the system in terms of the changes in pressure and temperature:

$$dv = \left( \frac{\partial v}{\partial P} \right)_T dP + \left( \frac{\partial v}{\partial T} \right)_P dT. \quad (1.37)$$

If we look at the last equation carefully, we recognize a term which looks very similar to the thermal coefficient of volume expansion,  $\beta$ , which we defined earlier as

$$\beta = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P \quad (1.38)$$

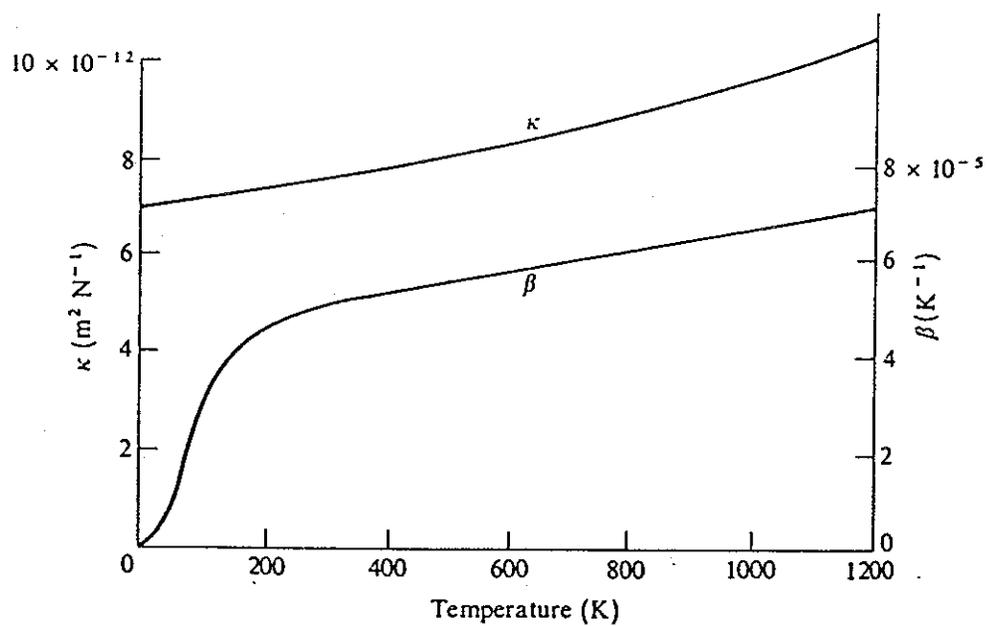


Fig. 1.15. The isothermal compressibility  $\kappa$  and the thermal coefficient of volume expansion  $\beta$  of copper as functions of temperature at a constant pressure of 1 atm.

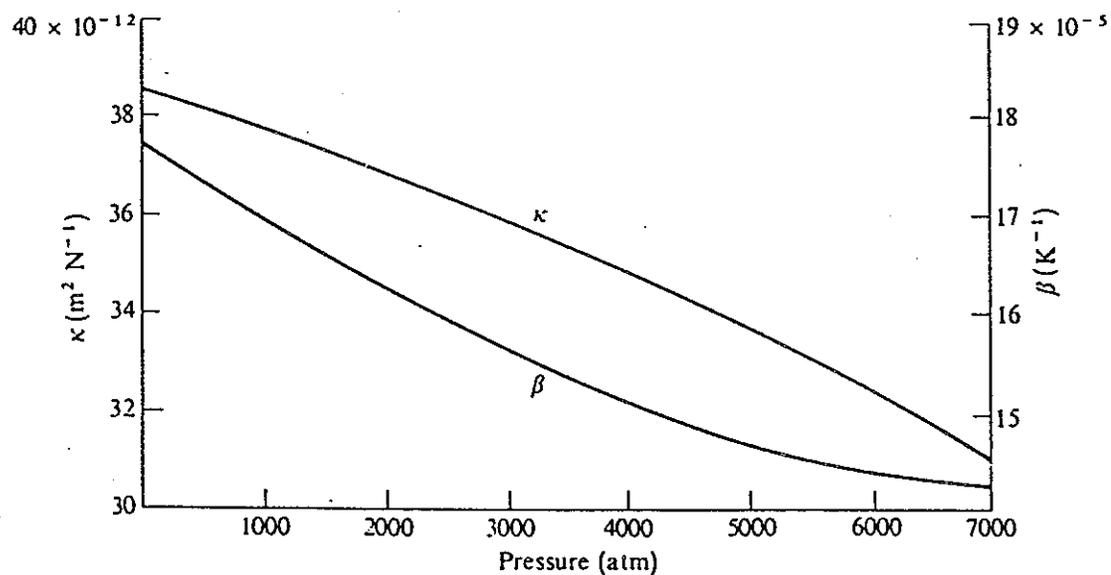


Fig. 1.16. The isothermal compressibility  $\kappa$  and the thermal coefficient of volume expansion  $\beta$  of mercury as functions of pressure at a constant temperature of 0°C.

The thermal coefficient of volume expansion  $\beta$  can be experimentally determined in the laboratory for different values of the pressure and temperature. Thus, even if we may not know a mathematical expression which is valid for all possible values of  $P$ ,  $v$ , and  $T$ , we can measure  $\beta$  over different ranges of  $P$ ,  $v$ , and  $T$  and form tables or graphs of  $\beta$  vs.  $P$ ,  $v$ , and  $T$  within certain regions of interest (as in Fig. 1.15 and 1.16). The second partial derivative in the  $dv$ -equation above is related to the isothermal compressibility,  $\kappa$ , which is *also* an experimentally measurable quantity, defined by the equation

$$\kappa = -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T \quad (1.39)$$

The minus sign in this equation is due to the fact that the quantity  $(\partial v/\partial P)_T$  is inherently negative, and we wish to define  $\kappa$  so that it is a positive quantity. Using these two experimentally measurable quantities, we can write

$$dv = -\kappa v dP + \beta v dT \quad (1.40)$$

or, dividing by  $v$ ,

$$dv/v = -\kappa dP + \beta dT, \quad (1.41)$$

which would allow us, if we knew the approximate values of  $\kappa$  and  $\beta$  (or their dependence upon  $P$  and  $T$ ), to integrate this equation over a finite change in volume for a finite change in pressure and temperature. This would allow us to determine the approximate equation of state for this particular substance in the region where we know the values of  $\kappa$  and  $\beta$ . To illustrate this process, we look at the following example.

**Example 1.1** Determination of the Equation of State when  $\kappa$  and  $\beta$  are known. Assume that we find that the constants  $\beta$  and  $\kappa$  are given experimentally by

$$\beta = 1/T \quad \text{and} \quad \kappa = 1/P \quad (1.42)$$

respectively (i.e.,  $\beta$  is a function of  $T$  only and  $\kappa$  is a function of  $P$  only, and these are inverse relationships). Then we can write

$$dv/v = -dP/P + dT/T, \quad (1.43)$$

which can be integrated between two different states A and B to give

$$\ln v_B - \ln v_A = -[\ln P_B - \ln P_A] + \ln T_B - \ln T_A, \quad (1.44)$$

or

$$\ln \left[ \frac{v_B}{v_A} \right] = -\ln \left[ \frac{P_B}{P_A} \right] + \ln \left[ \frac{T_B}{T_A} \right] \quad (1.45)$$

giving

$$\ln \left[ \frac{v_B}{v_A} \right] = \ln \left[ \frac{P_A T_B}{P_B T_A} \right] \quad (1.46)$$

or

$$\frac{v_B}{v_A} = \frac{P_A T_B}{P_B T_A} \quad (1.47)$$

or finally

$$(Pv/T)_A = (Pv/T)_B = \text{constant}, \quad (1.48)$$

which is the ideal gas law! We have, therefore, shown that if we can determine a functional relationship for  $\beta$  and  $\kappa$ , we can, in principle, determine the equation of state of the system.

**RELATIONSHIPS BETWEEN THE PARTIAL DERIVATIVES OF STATE VARIABLES**

We showed earlier that changes in the state variables can be written:

$$dP = \left(\frac{\partial P}{\partial v}\right)_T dv + \left(\frac{\partial P}{\partial T}\right)_v dT \quad (1.49)$$

$$dT = \left(\frac{\partial T}{\partial v}\right)_P dv + \left(\frac{\partial T}{\partial P}\right)_v dP, \quad (1.50)$$

and

$$dv = \left(\frac{\partial v}{\partial P}\right)_T dP + \left(\frac{\partial v}{\partial T}\right)_P dT. \quad (1.51)$$

We will show in what follows that once we determine any *two* of the partials in the equations above, we can determine any of the other four. This means that an experimental measurement of  $\kappa$  and  $\beta$  (valid in the region of interest) is all that is needed to determine the changes in pressure with volume and temperature, or changes in temperature with volume and pressure, etc.

It is important to note here that these equations are valid *only* because the variables  $P$ ,  $v$ , and  $T$  are *state* variables. This means that when a system is carried from state  $A$  to state  $B$  on a  $P, v, T$  surface and then, along a different path, back to state  $A$ , the state variables *will return to their initial values*. That is, the pressure, volume, and temperature measured at state  $A$  ( $P_A, V_A, T_A$ ) *do not depend upon how the system came to state A*. This statement is not generally true for *all* the quantities of interest in the study of thermodynamics, however. For example, a gas may do work on its surrounding as it expands. The amount of mechanical work done during such a process is given by the integral

$$W_{A \rightarrow B} = \int_A^B P \, dV \quad (1.52)$$

but, as we will show in the next chapter, *this integral depends upon the particular path taken from state A to state B*. Thus, *the work done in a given process depends upon the actual path taken, not just on the end points!* This is also true for the amount of heat added to, or removed from, a system. This means that an equation of the form

$$\text{NOT VALID *****} \quad dW = \left(\frac{\partial W}{\partial P}\right)_T dP + \left(\frac{\partial W}{\partial T}\right)_P dT \quad \text{***** NOT VALID}$$

*is not valid* since the change in work is actually *path dependent*. It is very important that one keeps clearly in mind the fact that some parameters are *state variables* (these are not path dependent), while others are not. To help us distinguish between changes in state variables and changes in other variables, we will write the differential change in a state variable as  $dE$  (or  $dP$  or  $dT$ ), but the change in a variable which is *not* a state variable as  $\delta W$  (or  $\delta Q$ ).

Now, let's demonstrate how the different partial derivatives are related to one another. We begin with the equation

$$dv = \left(\frac{\partial v}{\partial P}\right)_T dP + \left(\frac{\partial v}{\partial T}\right)_P dT \quad (1.53)$$

We can use the  $dP$  equation to substitute into this equation to give

$$dv = \left(\frac{\partial v}{\partial P}\right)_T \left[ \left(\frac{\partial P}{\partial v}\right)_T dv + \left(\frac{\partial P}{\partial T}\right)_v dT \right] + \left(\frac{\partial v}{\partial T}\right)_P dT \quad (1.54)$$

or

$$dv = \left[ \left(\frac{\partial v}{\partial T}\right)_P + \left(\frac{\partial v}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_v \right] dT + \left(\frac{\partial v}{\partial P}\right)_T \left(\frac{\partial P}{\partial v}\right)_T dv \quad (1.55)$$

Subtracting the last term on the right from both sides of the equation gives

$$\left[1 - \left(\frac{\partial v}{\partial P}\right)_T \left(\frac{\partial P}{\partial v}\right)_T\right] dv = \left[\left(\frac{\partial v}{\partial T}\right)_P + \left(\frac{\partial v}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V\right] dT \quad (1.56)$$

Since this equation is valid for *any* process on the  $P, v, T$  surface, it must be valid for an isothermal process in which  $dT = 0$ . This would mean that the left hand side of this last equation must be identically zero, or

$$1 - \left(\frac{\partial v}{\partial P}\right)_T \left(\frac{\partial P}{\partial v}\right)_T = 0 \quad (1.57)$$

since the volume change in a given process cannot be zero at the same time that the temperature change is zero. [If *both*  $dv$  and  $dT$  were zero, the state could not change at all! From the ideal gas equation, if  $T$  is held constant a change in state of the system means that both  $P$  and  $v$  must change by some amount. If either  $P$  or  $v$  is held constant in an isothermal process, the other must also remain constant, so that the state of the system does not change.] This last equation gives us the so-called “reciprocal rule” for partial derivatives:

$$\boxed{\left(\frac{\partial v}{\partial P}\right)_T = \frac{1}{\left(\frac{\partial P}{\partial v}\right)_T}} \quad (1.58)$$

Similarly, if we look back at Equ. 1.56 and follow an isochoric process (i.e., one in which  $dv = 0$ ), we have

$$\left(\frac{\partial v}{\partial T}\right)_P + \left(\frac{\partial v}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = 0 \quad (1.59)$$

or

$$\left(\frac{\partial v}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = - \left(\frac{\partial v}{\partial T}\right)_P \quad (1.60)$$

and, using the reciprocal rule demonstrated above, the right hand term can be “inverted” and multiplied so that the equation becomes the so-called “cyclic rule” for partial derivatives:

$$\boxed{\left(\frac{\partial T}{\partial v}\right)_P \left(\frac{\partial v}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = -1} \quad (1.61)$$

In the equation above, notice that the denominator must match the adjacent numerator in the terms on the left side of the equation, and that *the actual ordering of the terms is irrelevant*.

Using the two boxed equations, one can show that if we know just two of the partial derivatives, we can obtain all the other partial derivatives. The following examples demonstrate how these two rules may be applied.

**Example 1.2** We assume that we can determine the isothermal compressibility and the volume coefficient of thermal expansion:

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P \quad \text{and} \quad \kappa = - \frac{1}{v} \left(\frac{\partial v}{\partial P}\right)_T$$

in the laboratory. If we want a general equation for  $dP$  in terms of the changes in temperature and volume, we can write:

$$dP = \left(\frac{\partial P}{\partial v}\right)_T dv + \left(\frac{\partial P}{\partial T}\right)_V dT$$

From the reciprocal rule, the first term on the right can be expressed as

$$\left(\frac{\partial P}{\partial v}\right)_T = 1/\left(\frac{\partial v}{\partial P}\right)_T = -1/\kappa v \quad (1.62)$$

The second term on the right can be written in a slightly different form by using the cyclic relationship

$$\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_P \left(\frac{\partial v}{\partial P}\right)_T = -1$$

which gives

$$\left(\frac{\partial P}{\partial T}\right)_v = - \left(\frac{\partial v}{\partial T}\right)_P / \left(\frac{\partial v}{\partial P}\right)_T$$

Thus, the partial of pressure with respect to temperature at constant volume is related to the isothermal compressibility  $\kappa$  and to the thermal coefficient of expansion at constant pressure  $\beta$  by the equation

$$\left(\frac{\partial P}{\partial T}\right)_v = - \beta v / [-\kappa v] = \beta / \kappa \quad (1.63)$$

We can therefore express the change in pressure of a system in the following way:

$$dP = - \frac{1}{\kappa v} dv + \frac{\beta}{\kappa} dT \quad (1.64)$$

from which we can calculate the change in pressure of the system in going from state  $A$  to state  $B$  if we know the difference in the specific volume and in the temperature of these two states, and if we know the functional dependence of  $\beta$  and  $\kappa$  on the temperature and on the specific volume (see Figs. 1.15 and 1.16).

**Example 1.3** Lets try to evaluate  $\beta$  for a Van der Waal's gas. (We showed earlier that  $\beta$  for an *ideal* gas was given by  $\beta = 1/T$ .) Again, the defining equation for  $\beta$  is

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P$$

Now the Van der Waal's equation is given by

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT,$$

which is a cubic in  $v$ , so that the evaluation of  $dv/dT$  is non-trivial. However, we can express the coefficient of thermal expansion, using the reciprocity and cyclic rules in terms of other partials which are more easily evaluated. Thus, we want to express  $(\partial v/\partial T)_P$  in terms of  $(\partial P/\partial T)_v$  and  $(\partial P/\partial v)_T$ . Using the cyclic relation

$$\left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_v \left(\frac{\partial P}{\partial v}\right)_T = -1$$

we can write

$$\left(\frac{\partial v}{\partial T}\right)_P = - \frac{\left(\frac{\partial P}{\partial T}\right)_v}{\left(\frac{\partial P}{\partial v}\right)_T}$$

We can fairly easily solve Van der Waal's equation for the pressure  $P$ , to get

$$P = \frac{RT}{(v - b)} - \frac{a}{v^2}$$

The partials of the pressure are

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b}$$

and

$$\left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3}$$

Dividing this last equation by the former one, we obtain, upon simplification,

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_P = \frac{R v^3 (v-b)}{R T v^3 - 2 a (v-b)^2} \quad (1.65)$$

for a Van der Waal's gas. You should verify that this expression reduces to the expected result (the ideal gas result) as  $v \rightarrow \infty$ .