

INTRODUCTION

1.1 THE SCIENCE OF THERMODYNAMICS

Thermodynamics is concerned with the study of energy transformations and the relationship of these transformations to materials properties. These relationships are derived from *thermodynamic laws*, which are mathematical expressions assumed to hold true for all cases in which the specified conditions of the law are met experimentally. Because its laws are independent of atomic and molecular theory, *classical thermodynamics* can be thought of as a *macroscopic science*.

The purpose of thermodynamics is to predict changes in the properties of some finite portion of space set aside for investigation and to determine the influence, if any, on this portion of space by its surroundings. In the engineering and physical sciences, thermodynamics is used to assess efficiency and predict the occurrence of chemical and physical processes. Unfortunately, thermodynamics generally cannot be used to determine the rate at which a reaction takes place—i.e., it tells what occurs at equilibrium, but not when.

1.2 SYSTEMS, SURROUNDINGS, AND PHASES

Thermodynamic analysis starts with identification of the *system* under study and the location of its boundaries relative to the *surroundings*. For example, materials systems are composed of *phases* in a finite portion of space set aside for investigation. A phase is a physically distinct, mechanically separable portion of a system, e.g., ice in a mixture of ice and water or the mineral olivine in the olivine basaltic rocks of the Hawaiian Islands. Systems composed of one phase are said to be *homogeneous*, while systems composed of two or more phases are said to be *heterogeneous*. The boundaries of a system may be real, such as the walls of a container holding a metal charge, or they may be purely imaginary. Everything outside the system, which either directly influences or has no influence at all on its behavior, constitutes the surroundings. If a system is unaffected by its surroundings it is said to be *isolated*. An isolated system exchanges neither energy nor mass with its surroundings. A *closed system* exchanges only energy with its surroundings whereas an *open system* exchanges both energy and mass with its surroundings.

1.3 MACROSCOPIC STATE OF A SYSTEM

Experimental measurement of thermodynamic properties provides the basis for the complete description of the *macroscopic* state of a system. Hence, the empirical approach is the primary focus of this book. The number of *macroscopic coordinates* or variables needed to define a system depends upon whether the system is open or closed and upon the identity of the boundary between the system and the surroundings. For example, the mineral phases comprising a rock at great depth in the earth's crust may react to form other

minerals upon exhumation to the surface. If the exhumed rock is considered the system, the pressure, temperature, and composition recorded under exhumed conditions may be adequate to describe the state of the system at or near the surface. However, if the focus of attention is reaction conditions at some specific point in time at great depth, then an entirely different set of pressure, temperature, and composition data is required. The *macroscopic state of a system* refers to the experimental coordinates needed to define the system in such a manner that it could be duplicated. If the coordinates change in any way, the system is said to undergo a *change in state*. For example, the state of a closed system can be defined by any two of three macroscopic variables: namely, pressure, volume, and temperature. Hence, if one of these is selected as the dependent variable, the other two become the independent variables. If the system undergoes a change in one or more independent variables, it changes state. Microscopic states and their connection to macrostates, briefly discussed in Chapter 3, are the subject matter of statistical thermodynamics.

1.4 EQUILIBRIUM

A system is said to be in a *state of equilibrium* when there is no perceptible change in macroscopic coordinates with time. Such systems *appear* to be at rest. A system in *chemical equilibrium* appears to be at rest but actually involves a balance of reactions opposing one another at equal rates. The equilibrium between a gas and a liquid at the boiling point of the liquid and between a solute and its undissolved supersaturated component are examples of chemical equilibrium.

In addition to chemical equilibrium, systems may exhibit mechanical and thermal equilibrium. A system is said to be in a state of *mechanical equilibrium* when no unbalanced force exists between the internal parts of the system as well as between the system and its surroundings. *Thermal equilibrium* occurs when a system and its surroundings are at the same temperature and no net heat transfer occurs across the boundary.

Any system in chemical, mechanical, and thermal equilibrium is said to be in a state of *thermodynamic equilibrium*. Such systems can be described in terms of time-independent macroscopic coordinates. It should be noted that a system at *steady state* can be described in terms of time-independent macroscopic coordinates, but it is not at equilibrium because the coordinates change if the surroundings are modified. Some equilibrium states can be predicted from everyday observations. For example, it is intuitively known that when a bar of hot metal is quenched in water, the metal and the water reach thermal equilibrium at an intermediate temperature. In more complex systems, the equilibrium state is not predictable from observation, and analytic criteria for equilibrium must be established. Establishing such criteria is important, for example, in order to determine the direction in which a chemical reaction will spontaneously proceed at some instant in time when the macroscopic coordinates of the chemical system are known. A summary of the preceding discus-

sion is presented in Table 1.1.

Table 1.1: Thermodynamic Equilibrium States of A System

<i>Thermodynamic Equilibrium</i>		
<i>I. Chemical Equilibrium:</i>	<i>II. Mechanical Equilibrium:</i>	<i>III. Thermal Equilibrium:</i>
Balance of opposing reactions at equal rates	No unbalanced force in the system or between the system and its surroundings	System is at the same temperature as the surroundings

1.5 ADIABATIC AND DIATHERMIC BOUNDARIES

Two types of boundaries, often distinguished in thermodynamics, are *adiabatic** and *diathermic*. Adiabatic boundaries or heat insulators prevent heat transfer between a system and surroundings. Diathermic boundaries or heat conductors allow a system to exchange heat with its surroundings and, in so doing, are themselves influenced during the interaction.

Suppose two or more systems are connected by an adiabatic boundary to each other and by a diathermic boundary to an additional system as in Figure 1.1(a). If this configuration is itself enclosed by an adiabatic boundary, then it can be concluded that the adiabatically connected systems will be in thermal equilibrium with the additional system. If the adiabatic boundary separating the systems is removed and replaced by a diathermic boundary at the same temperature as the original boundary, all systems will be in thermal equilibrium with each other, e.g., Figure 1.1(b). Zemansky and Van Ness (1966, p. 7) expressed these observations as the *Zeroth Law of Thermodynamics*: "Two systems in thermal equilibrium with a third are in thermal equilibrium with each other." The reader is also referred to Thomsen (1962) for an interesting discussion of the Zeroth Law.

* Although there is no such thing as a perfect adiabatic heat insulator, experiments may be carried out so as to closely approximate adiabatic conditions for the duration of the experiment.

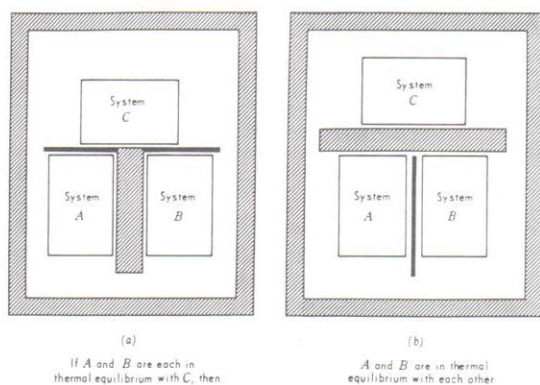


Figure 1.1 Illustration of the Zeroth Law of Thermodynamics. Cross shading indicates adiabatic boundaries; thick dark lines, diathermic boundaries. (From M.W. Zemansky and H.C. Van Ness, 1966, *Basic Engineering Thermodynamics*, Fig. 1.2. Reprinted by permission of McGraw-Hill, Inc., New York.)

1.6 IRREVERSIBLE AND REVERSIBLE PROCESSES

Changes in state take place by *irreversible* or *reversible processes*. An irreversible process, also known as a *spontaneous* or *natural process*, is one in which a system moves from a nonequilibrium state to one of equilibrium as a consequence of some finite external agent or driving force acting on the system. Although it is natural for all nonequilibrium systems to move toward an equilibrium state, the rate at which the drive towards equilibrium occurs is variable. The freezing of granitic magma intruded into the earth's crust, for example, is a *thermally irreversible* process that can vary from a fraction of a second at the surface of the intrusion to many millions of years deep inside of it. The external agent causing the change in state of the intrusion is the thermal gradient between the magma and the cooler surroundings. An example of *mechanical irreversibility* is the free expansion of a gas from its container into a vacuum as a consequence of differential pressure between the gas and the vacuum. Other examples of spontaneous processes include those displaying *chemical irreversibility*. These include changes in chemical composition (*chemical reactions*), changes in crystal structure but not composition (*polymorphic or allotropic transformations*), phase changes, and the mixing of substances.

A reversible process, also referred to as a *quasi-static process*, is one in which system properties change due to an infinitesimally small driving force that never produces more than an infinitesimally small displacement from equilibrium. In addition, any change in the system can be reversed by an infinitesimally small change in the driving force. The system can be thought of as passing through a continuum of equilibrium states in such a manner that each infinitesimally small deviation from equilibrium is followed by an equilibrium state.

1.7 PATH INDEPENDENT PROPERTIES, CHANGE IN STATE, AND CYCLIC PROCESSES

It is convenient to express the properties of a system (or its surroundings) in terms of algebraic variables. In the literature, *path independent* properties or variables are referred to by numerous names including: thermodynamic functions, thermodynamic functions of state, thermodynamic variables, thermodynamic properties, state functions, state variables, state properties and point functions.

If θ is a state variable with initial and final values θ_i and θ_f respectively, the change in state of a system with respect to θ is designated as $\Delta\theta = \theta_f - \theta_i$. An infinitesimal change in θ between the initial and final states of the system is designated by the *exact differential* $d\theta$. The symbols Δ and d are used to designate macroscopic or infinitesimal changes respectively, for state functions only.

If the initial state (i) of a system is identical to its final state (f), then a combination of processes that takes the system through a series of changes from i to f is said to be a *cyclic process* or a *cycle*. For any state function θ that has gone through n cycles, where n is an integer > 0 ,

$$\sum_{a=1}^n \Delta\theta_a = 0 \quad \text{or} \quad \oint d\theta = 0$$

where \oint designates a *cyclic integral*. An example of a mechanical system that undergoes thousands of cyclic processes per second is the fluid in the power steering pump of an automobile engine. If the engine is properly tuned, the thermodynamic properties of the fluid as it enters the high pressure hose are the same as when it reenters this hose after having first passed through the steering gear box into the return hose and then into the pump reservoir.

State properties are classified as either *extensive* or *intensive*. Extensive properties are characterized by magnitudes dependent on the size of a system or system component. They are often expressed with a superscript prime and include such properties as mass (m), volume (V'), and as will be seen later, internal energy (U'), enthalpy (H'), entropy (S'), Gibbs free energy (G'), and total heat capacity (C'). Intensive properties are macroscopic coordinates characterized by magnitudes independent of the size of a system or a system component. They include pressure (P), temperature (T), stress (σ), strain (ϵ), surface tension (γ), electric cell Emf (E), specific volume (v), density (ρ), molar heat capacity (C), specific heat capacity (c), volume (V), internal energy (U), enthalpy (H), entropy (S), and Gibbs free energy (G). Intensive properties may be derived from extensive properties by expressing the extensive property on a per unit mass (*specific*), mole, or volume basis. For example, V' , the volume of a system component is an extensive thermodynamic property. Dividing volume by the mass or the number of moles, the result is an intensive property such as specific volume (V'/mass) = v or molar volume (V'/moles) = V .

The path independent nature of thermodynamic properties is illustrated in Figure 1.2. Point 1 (initial state) is defined by P_1 , V_1 , and T_1 , while point 2 (final state) is defined by P_2 , V_2 , and T_2 . Since both points are represented by state properties, the change in these properties is the same for any process or transition path that leads from point 1 to 2. The transition paths, for example, may be characterized by *isothermal* ($\Delta T = 0$), *isochoric* or *isometric* ($\Delta V = 0$), or *isobaric* ($\Delta P = 0$) processes. Each path will result in the same values for P_2 , V_2 , and T_2 at point 2. As illustrated, the paths can be expressed in terms of partial derivatives. Mathematical manipulation of these partial derivatives in conjunction with the appropriate equation of state and thermodynamic relations given in Chapter 4 are useful in computing other desired property changes.

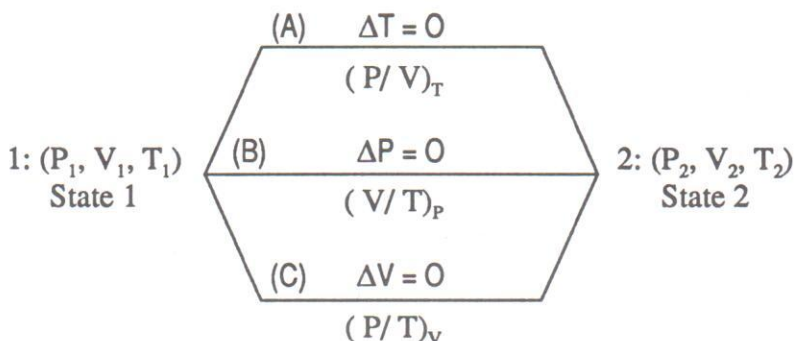


Figure 1.2 Illustration of the path independent nature of state properties represented by points 1 and 2. Changes in P , V , and T are the same for any arbitrary process leading from point 1 to 2, i.e., the values at point 2 are the same regardless of the path between the points. Isothermal (path A), isobaric (path B), and isochoric (path C) processes, represented by arbitrarily drawn lines, can be expressed in terms of partial derivatives.

Closed thermodynamic systems can be described by three state properties in which any one is a function of the other two. P , V , and T are the state variables most commonly used to define a system because P , V , and T are amenable to direct experimental measurement. If T and V are known, P is fixed and the *dependent variable* P is a state property of the *independent variables* V and T , or $P = f_1(V, T)$. Alternately, $T = f_2(V, P)$ or $V = f_3(P, T)$.

1.8 EQUATION OF STATE AND THE CONDITION OF EXACTNESS

An *equation of state* is used to quantify a state property of a specific substance in terms of other state properties. Equations of state are primarily empirically derived and can be used with confidence only within the range of measured parameters and limits of experimental error for which they were determined.

The equation of state for an *ideal gas* relates P, V , and T by the relationship

$$PV' = nRT \quad [1-1]$$

where n is the number of moles. This equation is applicable at lower pressures, usually below about 5 atm, and at temperatures dependent upon the particular gas. For condensed states, three useful equations of state are the *volume thermal expansion coefficient*, α , defined by

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad [1-2]$$

the *isothermal compressibility coefficient*, β , defined by

$$\beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad [1-3]$$

and *Hooke's law*, defined by $\sigma = \epsilon E$ where σ is stress, ϵ is strain, and E is *Young's modulus*. Values of α and β for selected substances are given in Appendix B, Tables B.1 and B.2.

Consider a system that undergoes an infinitesimal change of state. Since state changes are path independent, corresponding infinitesimals are path independent also, i.e., exact differentials. For example, if a state variable z is functionally expressed by

$$z = f(x_1, x_2, \dots, x_n),$$

a theorem derived from the chain rule for partial derivatives then gives

$$dz = \left(\frac{\partial z}{\partial x_1} \right)_{x_2, \dots, x_n} dx_1 + \left(\frac{\partial z}{\partial x_2} \right)_{x_1, x_3, \dots, x_n} dx_2 + \dots + \left(\frac{\partial z}{\partial x_n} \right)_{x_1, \dots, x_{n-1}} dx_n \quad [1-4]$$

where each partial derivative is itself a function of x_1, \dots, x_n . The terms

$$\left(\frac{\partial z}{\partial x_1} \right)_{x_2, \dots, x_n}, \dots, \left(\frac{\partial z}{\partial x_n} \right)_{x_1, \dots, x_{n-1}}$$

are called the *partial differentials* of z with respect to x_1, x_2, \dots, x_n respectively. The sum of the partial differentials, denoted as dz is the *total differential*. As an example, consider the change in internal energy of an ideal gas as a function of temperature and volume. Beginning with $U = f(V, T)$, the total differential is

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV.$$

For the specific case of an ideal gas, $(\partial U / \partial V)_T = 0$; hence $U = f(T)$ and only the

first term is finite. For materials behavior in general, such a simplification would be incorrect. A thermodynamic property, z , that can be expressed in the form of [1-4], is defined in differential calculus as an exact differential.

An important property of exact differentials can now be derived by considering the case where $z = f(x,y)$. The result can be extended to functions of any number of independent variables. If a function f is defined by the relation $z = f(x,y)$,

$$dz = \left(\frac{\partial z}{\partial x} \right)_Y dx + \left(\frac{\partial z}{\partial y} \right)_X dy.$$

Now let $M = M(x,y) = \left(\frac{\partial z}{\partial x} \right)_Y$ and $N = N(x,y) = \left(\frac{\partial z}{\partial y} \right)_X$, then

$$dz = M(x,y)dx + N(x,y)dy.$$

Taking the partial derivative of M and N with respect to y and x respectively,

$$\left(\frac{\partial M(x,y)}{\partial y} \right)_X = \left(\frac{\partial}{\partial y} \left(\frac{\partial z}{\partial x} \right)_Y \right)_X$$

and

$$\left(\frac{\partial N(x,y)}{\partial x} \right)_Y = \left(\frac{\partial}{\partial x} \left(\frac{\partial z}{\partial y} \right)_X \right)_Y$$

The two derivatives on the right side of these last two equations are equal because the order of partial differentiation may be reversed according to a theorem from partial differential calculus (Protter and Morrey, 1970, p. 736). It follows that

$$\left(\frac{\partial M}{\partial y} \right)_X = \left(\frac{\partial N}{\partial x} \right)_Y \quad [1-5]$$

[1-5] is known as the *condition for an exact differential* and is a necessary characteristic of a thermodynamic property. By contrast, an infinitesimal that is not the differential of a function is called an inexact differential and cannot be expressed in the form of [1-5].

1.9 PATH DEPENDENT PROCESSES: WORK AND HEAT

Unlike thermodynamic properties, *path dependent* variables are characterized by the fact that the change in the variable is contingent upon the specific path taken between states. Such variables can be thought of as process variables because numerical values are determined for the process. Path dependent

variables are designated by attaching the prefix "non" to the path independent names, e.g., nonstate function or nonthermodynamic property. Work (W) and heat (Q) are two such examples. Neither can be expressed as an *exact differential*. For this reason, infinitesimals of W and Q are indicated as *inexact differentials* by using the symbol δ . The inexact differentials* of W and Q are thus written as δW and δQ respectively. It is important to note that it is improper to use such phrases as the "work contained in the body" or the "heat contained in the body." Work and heat are path dependent energy transfer processes and cannot be represented as exact differentials or point functions.

In the applications discussed in this book, only mechanical work or work against pressure will be considered. Other forms of work such as electrical, interfacial and gravitational will not be considered.

Work: Quasi-Static Tension or Compression of a Bar

When a bar, subjected to uniaxial elastic tension or compression, changes length from l to $l + dl$ where l is the original length of the bar, an infinitesimal amount of the total work performed by the axial load F applied to the bar is given by

$$\delta W' = -Fdl \quad [1-6]$$

In integrated form,

$$W' = - \int_{l_1}^{l_2} Fdl$$

where F is positive for tensile loading and negative for compressive loading as shown in Figure 1.3. The minus sign is inserted here for consistency with the conventions used in this book that *work done on a system is negative*, while *work done by a system is positive*.

Since the average uniaxial *engineering stress* on a bar of *original* cross-sectional area A is $\sigma = F/A$ and the infinitesimal strain associated with dl is $d\epsilon = dl/l$, substituting into [1-6] gives

$$\delta W' = -\sigma A l d\epsilon$$

Since $Al = V'$,

$$\delta W' = -\sigma V' d\epsilon \quad [1-7]$$

* An alternate symbol appearing in the literature for an inexact differential is \mathcal{A} . In this book, a δ will be used to indicate an inexact differential.

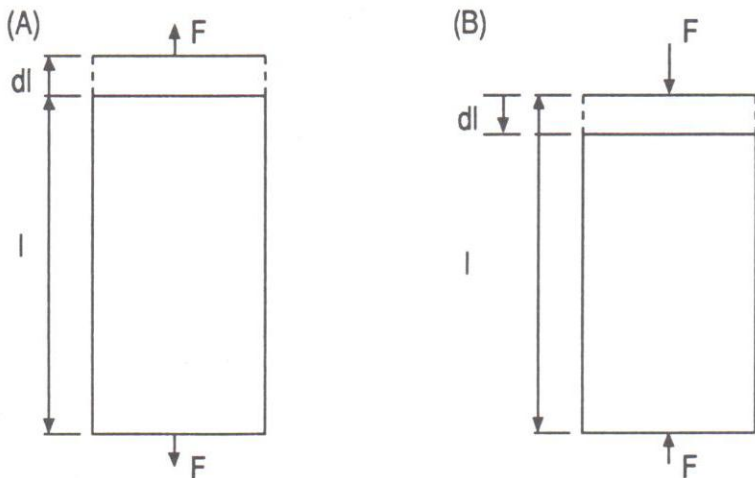


Figure 1.3 Uniaxial elastic deformation of a bar, originally of length l . (a) Tensile load F increases the length of the bar hence $W' < 0$. (b) Compressive load F decreases the length of the bar hence $W' < 0$. Negative W' agrees with the minus sign convention for the work done *on* a system.

The reader can verify the dimensional accuracy of [1-7] by substituting units for σ , V' , and $d\epsilon$.

Assuming that the change in V' during elastic deformation is small enough to be neglected, the work done per unit volume of the bar for a finite change in strain from ϵ_1 to ϵ_2 is found by integrating [1-7],

$$W = - \int_{\epsilon_1}^{\epsilon_2} \sigma d\epsilon \quad (\text{work per unit volume}) \quad [1-8]$$

In order to evaluate [1-8], the functional relationship between σ and ϵ must be known. This relationship is not readily determined if any point in the bar undergoes accelerated motion during tensile or compressive loading because both σ and ϵ would then be functions of time. If the external load or driving force F is slowly increased, a quasi-static process is approximated, and Hooke's law, $\sigma = \epsilon E$, can be substituted into equation [1-8] to give

$$W = -E \int_{\epsilon_1}^{\epsilon_2} \epsilon d\epsilon \quad [1-9]$$

where E , Young's Modulus, for the material comprising the bar is available for many materials. Equations [1-8] and [1-9] are not valid above the yield point of the material since irreversible deformation will occur.

Figure 1.4 illustrates experimentally derived first cycle stress-strain loops for a magnesium alloy (Dowmetal A-T4) subjected to uniaxial tensile loading. The work done per unit volume of the bar stressed from state 1 to state 2 on the original first cycle curve is the shaded area under this curve between points 1 and 2.

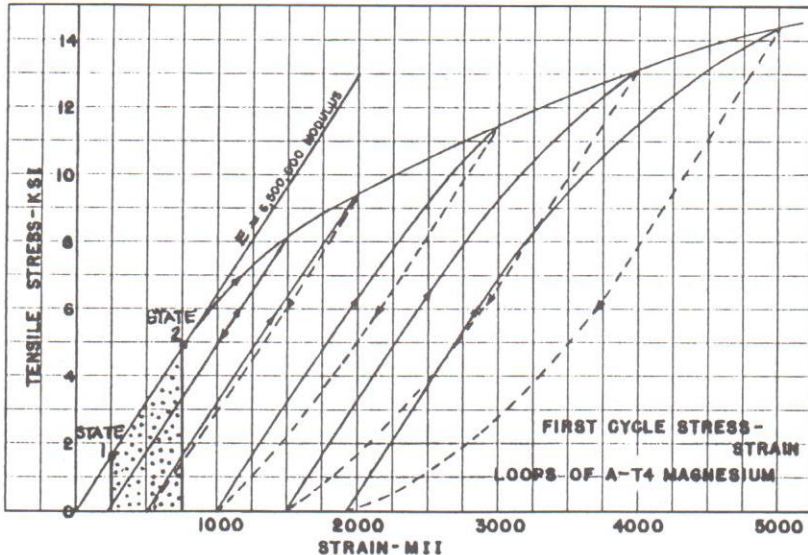


Figure 1.4 Experimentally derived uniaxial tensile first cycle stress-strain loops for Dowmetal A-T4 magnesium alloy. The work done per unit volume of the alloy during the change from state 1 to state 2 on the first loop is the shaded area shown. Equation [1-8] applies only to partial loop segments parallel to the 6.5×10^6 psi modulus slope since otherwise, irreversible permanent deformation occurs. MII = microinches per inch (From M.H. Polzin, 1951, Fig. 9 with modifications. Reprinted by permission of the Society for Experimental Mechanics, Inc., Bethel, CT.)

Example Problem 1-1

Prior to loading, the original circular cross-sectional area of a 5 m long brass bar measures 76.2 mm in diameter. After the bar is loaded in compression to 120 kip, the compressive stress is increased isothermally and quasi-statically to an engineering stress of 45 ksi.

- Compute the total work done as a result of increasing the stress to 45 ksi from the initial load of 120 kip. $E_{\text{Brass}} = 15 \times 10^6$ psi. State assumptions made in the calculation.
- What is the significance of the sign associated with the the work performed?

Solution(a) Substituting $\epsilon E = \sigma$ into [1-7],

$$W' = -EV' \int_{\epsilon_1}^{\epsilon_2} \epsilon d\epsilon = -\frac{EV'}{2} (\epsilon_2^2 - \epsilon_1^2). \text{ Substituting } \epsilon = \frac{\sigma}{E},$$

$$W' = -\frac{V'}{2E} (\sigma_2^2 - \sigma_1^2).$$

Since $V' = \pi r^2 l$ for a cylinder of radius r and length l ,

$$V' = 3.14 \times \left(\frac{76.2}{2 \times 25.4} \right)^2 \times 5 \times 3.281 \times 12 \text{ in}^3 = 1391 \text{ in}^3.$$

Substituting $E = 15 \times 10^6 \text{ lb}_f/\text{in}^2$, $\sigma_2 = 45 \times 10^3 \text{ psi}$, and

$$\sigma_1 = \frac{120,000}{3.14} \times \left(\frac{2 \times 25.4}{76.2} \right)^2 \text{ psi} = 16,985 \text{ psi},$$

$$W' = \frac{-1391(45^2 - 16.985^2) \times 10^6}{2(15 \times 10^6) \times 12} \text{ ft} \cdot \text{lb}_f = \underline{\underline{-6710 \text{ ft} \cdot \text{lb}_f}}.$$

Assumption: $V' \neq f(\epsilon)$.(b) $W' = -$, hence work was done *on* the system (brass bar).**Work: Quasi-Static Pressure-Volume Expansion or Compression**

Figure 1.5 illustrates a *PVT* system* comprised of a gas inside a piston-cylinder arrangement. Suppose the cross-sectional area of the cylinder is A . In addition, suppose the gas in the cylinder is compressed by pushing the piston further into the cylinder and expanded when the gas pushes the piston in the opposite direction. If P is the pressure at the system-piston interface, the net force at this interface is $F = PA$. When the piston moves an infinitesimal distance dx , the work performed is equal to

$$\delta W = F \cdot dx/n \text{ or } \delta W = PA \cdot dx/n$$

* A *PVT* system is a *closed system* described by the macroscopic coordinates P , V , and T .

where n is the number of moles of the gas. Since $A dx/n = dV$,

$$\delta W = PdV \quad [1-10]$$

Integrating [1-10],

$$W = \int_{V_1}^{V_2} PdV \quad [1-11]$$

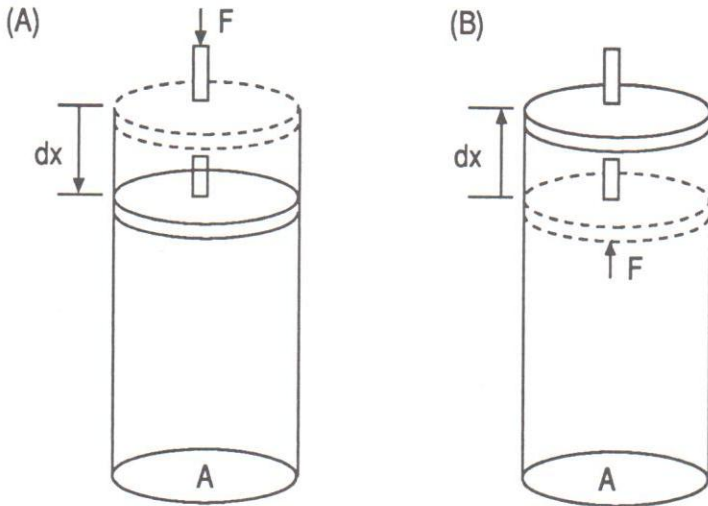


Figure 1.5 Compression of a gas (a) and expansion of a gas (b) during the motion of a piston in a frictionless cylinder of cross-sectional area A . The force, F , displaces the piston by dx . The work performed is given by [1-11].

If the piston moves with accelerated motion, both P and V are functions of time, and the computation becomes a problem in dynamics. However, if the piston moves slowly in either direction, the system approaches quasi-static expansion or compression as given by equation [1-11]. If T is constant or can be expressed as a function of V during these reversible processes, P becomes a function of V only and the calculations for work become mathematical problems involving integrals of the form

$$W = \int_{V_1}^{V_2} P(V)dV \quad (T \text{ constant}) \quad \text{or} \quad W = \int_{V_1}^{V_2} P(T(V))dV \quad (T = T(V)).$$

Example Problem 1-2

Six moles of an ideal gas at 100°C (373.16 K) undergo isothermal reversible expansion against a constant external pressure of 3.5 atm in a piston-cylinder apparatus. The volume of the gas is increased by a factor of 450%.

- (a) Compute the work performed as a result of the expansion.
 (b) Is the + sign for work consistent with convention?

Solution

- (a) The initial total volume V_1' of the gas is found from [1-1], the equation of state for an ideal gas: $PV' = nRT$. Conversion factors and the gas constant R used in this problem are found in the Table of Physical Constants and Conversion Factors preceding Chapter 1.

$$V_1' = \frac{6 \times 8.3144 \times 373.16}{3.5 \times 101,325} \text{ m}^3 = 52.492 \times 10^{-3} \text{ m}^3.$$

The final volume V_2 is

$$V_2' = 4.50 \times V_1' = 4.5 \times 52.492 \times 10^{-3} \text{ m}^3 = 236.214 \times 10^{-3} \text{ m}^3.$$

$$W' = \int_{V_1'}^{V_2'} P dV' = P(V_2' - V_1')$$

$$= 3.5 \times 101,325(236.214 - 52.492) \times 10^{-3} \\ = \underline{\underline{+65,155 \text{ J}}}.$$

- (b) The + sign associated with W' is consistent with convention since the gas system did work on the piston during expansion.

Work: Path Dependence

The path dependent nature of work is demonstrated in Example Problem 1-3 by considering the frictionless cylinder fitted with a movable piston illustrated in Figure 1.5. The initial state (1) and final state (4) of the gas are represented by the points (P_1, V_1, T_1) and (P_4, V_4, T_4) in Figure 1.6 respectively.

Example Problem 1-3

The purpose of this problem is two-fold. First, it illustrates the fact that work output is maximum for a reversible process. Secondly, it illustrates the fact that work output is dependent on path. In part (a), the path is chosen to be irreversible due to large and abrupt changes in P and V . In part (b), the path is chosen to be reversible or quasi-static by direct insertion of the equation of state (in this case the ideal gas law) into [1-11]. Note that the latter is closely (but not exactly) equivalent to placing a pile of sand grains on top of the piston and removing one grain at a time between state 1 and state 4. The

following data applies:

$n = 1$ kg mol of ideal gas, $T = 25^\circ\text{C}$ (constant temperature process).

Initial pressure: $P_1 = 100$ atm (State 1)

Process I: Release to 50 atm (State 2)

Process II: Release to 20 atm (State 3)

Process III: Release to 10 atm (State 4)

- (a) Calculate the work done during the irreversible expansion from state 1 to state 4.
- (b) Calculate the work done during the reversible expansion from state 1 to state 4. Note that the nearly analogous removal of 1 grain of sand reduces the pressure and corresponding volume only very slightly "one grain at a time."

Solution

(a) The data are plotted on Figure 1.6.

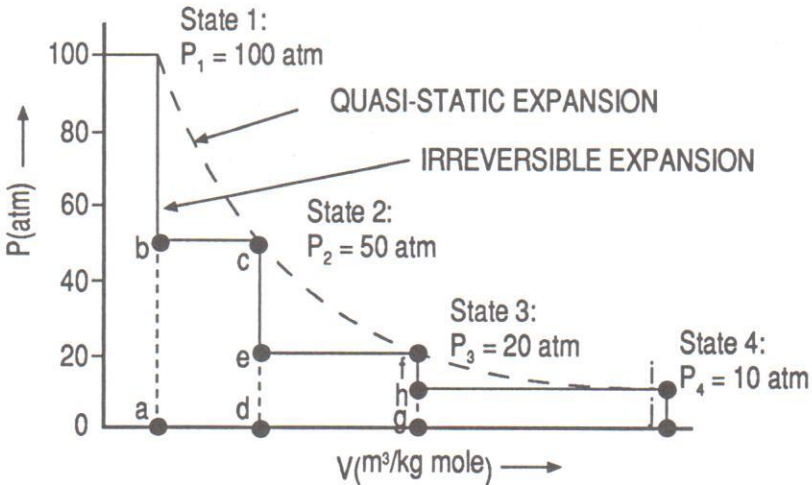


Figure 1.6 Reversible and irreversible expansion of an ideal gas.

$$V_1 = \frac{RT_1}{P_1} = \frac{8.3144 \text{ N} \cdot \text{m} \times 298 \text{ K} \times 1 \text{ atm}}{\text{kg mol} \cdot \text{K} \times 100 \text{ atm} \times 1.01325 \times 10^5 \text{ N/m}^2}$$

$$= 2.45 \times 10^{-4} \text{ m}^3/(\text{kg mol}).$$

$$V_2 = V_1 P_1 / P_2 = 2.45 \times 10^{-4} \times 2 = 4.9 \times 10^{-4} \text{ m}^3/(\text{kg mol}).$$

$$V_3 = V_1 P_1 / P_3 = 2.45 \times 10^{-4} \times 5 = 12.25 \times 10^{-4} \text{ m}^3/(\text{kg mol}).$$

$$V_4 = V_1 P_1 / P_4 = 2.45 \times 10^{-4} \times 10 = 24.5 \times 10^{-4} \text{ m}^3/(\text{kg mol}).$$

$$\begin{aligned}
 W &= \int_{V_1}^{V_4} P dV = \text{area abcd} + \text{area defg} + \text{area ghij}. \\
 &= [50 \times 10^{-4}(4.9 - 2.45) + 20 \times 10^{-4}(12.25 - 4.9) + 10 \times 10^{-4} \times \\
 &\quad (24.5 - 12.25)] = 0.0392 \text{ atm} \cdot \text{m}^3 / (\text{kg mol}) \\
 &= 0.0392 \times \frac{\text{atm} \cdot \text{m}^3}{\text{kg mol}} \times \frac{1.01325 \times 10^5 \text{ N}}{\text{atm} \cdot \text{m}^2} \times \frac{1 \text{ kN} \cdot \text{m}}{1000 \text{ N} \cdot \text{m}} \\
 &= \underline{3.972 \text{ kJ}/(\text{kg mol})}.
 \end{aligned}$$

$$\begin{aligned}
 \text{(b) } W &= \int_{V_1}^{V_4} P dV = RT \int_{V_1}^{V_4=10V_1} dV/V = 8.3144 \times 10^{-3} \times 298 \ln(10) \\
 &= \underline{5.705 \text{ kJ}/(\text{kg mol})}.
 \end{aligned}$$

The preceding results show that significantly more work would be accomplished if the expansion were carried out reversibly. Of course, such an expansion would be impossible because of frictional losses and time constraints.

Heat

Beginning in 1840, James Joule performed a number of experiments to determine the amount of work necessary to produce the same increase in the temperature of a system as a given amount of heat. This amount of work became known as the *mechanical equivalent of heat* and in order to determine its value, a unit of heat energy called the *calorie* was defined as the amount of heat required to raise the temperature of 1 gram of water from 14.5 to 15.5°C at 1 atm pressure. By performing mechanical as well as electrical work in adiabatically contained water, Joule determined the mechanical equivalent of heat to be 4.149 J/cal. This number was found to be completely independent of the type of work performed. The currently accepted value for the mechanical equivalent of heat (based on refined experimental techniques), known as the *thermochemical calorie*, is 4.184 J/cal.

The sign convention for describing heat transfer is: heat energy that flows *into* a body (*endothermic* process) is positive, while heat energy that flows *out* of a body (*exothermic* process) is negative.

The path-dependent nature of heat energy transfer between two thermodynamic states can be confirmed experimentally in the laboratory and is illustrated by Exercise Problem [3.5]. The similarity between Example Problem 1-3 and Exercise Problem [3.5] is illustrative of the process dependent nature of work and heat respectively, as discussed in the next chapter.

1.10 DISCUSSION QUESTIONS

- (1.1) Why is classical thermodynamics thought of as a macroscopic science?
- (1.2) Give examples of systems and corresponding surroundings.
- (1.3) Give examples of open and closed systems.
- (1.4) What is the meaning of the phrase "change in state"?
- (1.5) Give several examples of systems that are chemically irreversible.
- (1.6) What is a path independent property? Give examples and illustrate with drawings.
- (1.7) Define a cyclic process. Give an example.
- (1.8) Thermodynamic properties are "extensive" or "intensive." Define each and describe the relationship between them.
- (1.9) At the beginning of what turns out to be a very hot summer, you estimate the volume of water in a pond to be 840 m^3 . At the end of the summer, you estimate the volume of water to be 820 m^3 . After listening to the weather report every day from the time of your first to your last volume estimate, you determine that the average barometric pressure during this time was 745 mm Hg . If the decrease in water volume was entirely the result of evaporation, is there any meaning to calculating the work done during evaporation by using the volume change and pressure conditions given here?

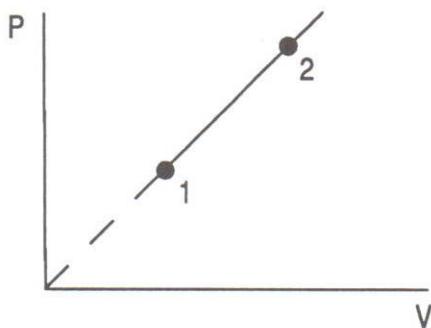
1.11 EXERCISE PROBLEMS

- [1.1] Calculate the coefficient of thermal expansion, α , at 273 K for an ideal gas.

Ans: $\alpha = 3.66 \times 10^{-3} \text{ K}^{-1}$.

- [1.2] Consider the reversible expansion process represented by the straight line 1-2 in the figure below. The working substance is 1 mole of an ideal gas. $P_1 = 1 \text{ atm}$, $P_2 = 2 \text{ atm}$, $V_2 = 2V_1$ and $T_1 = 300 \text{ K}$. Find W for the process.

Ans: $W = 3739 \text{ J/mol}$.



- [1.3] The generalized expression

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

can be used to calculate $C_p - C_v$ for any substance. Show that $C_p - C_v = R$ for an ideal gas.

- [1.4] An ideal gas undergoes an isobaric change from an initial State 1: (P_1, V_1', T_1) to a final State 2: (P_1, V_2', T_2) . Prove $V_2' - V_1' = (nR/P) \times (T_2 - T_1)$.

- [1.5] Show that the total work performed during the reversible isothermal expansion or compression of an ideal gas from a volume V_1' to V_2' is given by the equivalent expressions $W' = nRT \ln(V_2'/V_1')$ and $W' = nRT \ln(P_1/P_2)$.

- [1.6] The reading on a pressure gauge relative to vacuum is added to atmospheric pressure in order to determine absolute pressure, i.e., *absolute pressure = gauge pressure + atmospheric pressure*.

- (a) Calculate the work done by 10 moles of an ideal gas expanding reversibly from 58.784 to 14.696 psig (lb_f/in² gauge) in a piston-cylinder arrangement at a constant temperature of 125°F. Perform the calculation *without* using numerical gas volumes at absolute pressure. Express the answer in joules.

Ans: $W' \approx +24,750$ J.

- (b) Calculate the volume occupied by 10 moles of an ideal gas at 14.696 and 58.784 psig at a temperature of 125°F.

Ans: $V'_{14.696} = 0.133$ m³, $V'_{58.784} = 0.053$ m³.

- (c) Using the gas volumes obtained in (b), calculate the work done by 10 moles of an ideal gas expanding reversibly at a constant temperature of 125°F. Express the answer in joules. How does the answer compare to the one in (a)? Why are they the same or different?

Ans: $W' \approx +24,750$ J, the same as (a) because the path between identical initial and final states is the same.

- [1.7] Calculate the work done when the hydrostatic pressure on a cube of Cu measuring 2 cm on an edge is increased reversibly and isothermally at 0°C from 1 to 100 atm. Assume a negligible change in V over the pressure interval.

Ans: $W \approx -0.027$ J/mol.

- [1.8] Calculate the work done on the surroundings when one mole of liquid potassium expands to vapor reversibly and isothermally at 1000 K and 0.753 bar in a piston-cylinder arrangement.

Ans: $W = 7627$ kJ/kg mol.

- [1.9] Calculate the work done (internal compression) when a 350 lb mass of low carbon steel transforms from γ (austenite) to α (ferrite) during an air quench. Given that $V'_\gamma = 0.0486$ nm³ and $2V'_\alpha = 0.0493$ nm³, the

basis for these volumes is 4 atoms of iron (one unit cell of γ or two unit cells of α [Van Vlack, 1985, p. 76]).

$$\text{Ans: } W' = 30 \text{ J.}$$

- [1.10] Calculate the isobaric temperature change necessary to produce a molar volume change of $0.02 \text{ cm}^3/\text{mol}$ in a pyrope garnet, $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, crystal. Assume $\alpha V_{1 \text{ bar}, 298 \text{ K}}$ is constant over the temperature interval.

$$\text{Ans: } \Delta T = 6.71 \text{ K.}$$

- [1.11] Calculate the molar volume of the pyroxenoid wollastonite, CaSiO_3 , at a pressure of 200 bar and temperature of 298 K. Assume $\beta V_{1 \text{ bar}, 298 \text{ K}}$ is constant over the pressure interval. The initial pressure is 1 bar.

$$\text{Ans: } V = 39.92 \text{ cm}^3/\text{mol.}$$

- [1.12] Express $(\partial P/\partial T)_V$ in terms of the volume thermal expansion (α) and isothermal compressibility (β) coefficients of a mineral. Assume $\Delta\alpha$ and $\Delta\beta$ are negligible for small changes in P and T .

$$\text{Ans: } (\partial P/\partial T)_V = \alpha/\beta.$$

- [1.13] Calculate the pressure on a crystal of spinel, MgAl_2O_4 , heated isochorically from 273 to 308 K. The pressure at 273 K is 1 bar. Assume negligible changes in α and β over the P - T interval. The volume remains constant because of external constraint.

$$\text{Ans: } P_{308 \text{ K}} = 543 \text{ bar.}$$

- [1.14] A beam in a truss bridge is subject to uniaxial tension and compression (σ) in such a manner that the beam undergoes infinitesimal changes from one *thermodynamic equilibrium* state (T_1, σ_1) to another (T_2, σ_2) . The total differential of the dependent variable ε involves two parameters known from experiments to be nearly constant for small temperature changes. These parameters are the coefficient of linear thermal expansion α and Young's Modulus E . Mathematical definitions and additional experimental properties are as follows:

$$\alpha = \left(\frac{\partial \varepsilon}{\partial T} \right)_\sigma, \quad \alpha \text{ is nearly independent of } \sigma$$

$$E = \left(\frac{\partial \sigma}{\partial \varepsilon} \right)_T, \quad \text{for } \sigma < \text{the elastic proportional limit}$$

- (a) Write an equation of state for the beam as a functional relationship.

$$\text{Ans: } \varepsilon = f(T, \sigma).$$

- (b) Express the exact differential of ε in terms of α and E .

$$\text{Ans: } d\varepsilon = \alpha dT + (1/E)d\sigma.$$

- (c) Show that if ε is constant, $(\partial \sigma/\partial T)_\varepsilon = -\alpha E$.

- [1.15] Beginning with the expression $P = f(V, T)$

- (a) Express the total differential of P in terms of partial derivatives and name the partial differentials.

$$\text{Ans: } dP = \left(\frac{\partial P}{\partial V} \right)_T dV + \left(\frac{\partial P}{\partial T} \right)_V dT,$$

$$\text{partial differentials: } \left(\frac{\partial P}{\partial V} \right)_T dV, \left(\frac{\partial P}{\partial T} \right)_V dT.$$

(b) Use the condition of exactness to demonstrate that dP is an exact differential.

$$\text{Ans: } \frac{\partial^2 P}{\partial T \partial V} = \frac{\partial^2 P}{\partial V \partial T}, \text{ thus } dP \text{ is exact.}$$

[1.16] Uniaxial tensile first cycle stress-strain loops for the magnesium alloy Dowmetal A-T4 are illustrated below. Small partial cycles beginning at the lower end of each loop are on a constant slope of modulus $E = 6.5 \times 10^6$ ksi since the first part of each loop side is a line parallel to the original modulus line. For each such partial cycle, assume total elastic return upon the removal of stress. Compute the total work performed in $\text{ft} \cdot \text{lb}_f$ when a 10.0 in. long Dowmetal A-T4 cylinder of radius 2.50 in. undergoes the partial cycles for loops 1 and 2 shown.

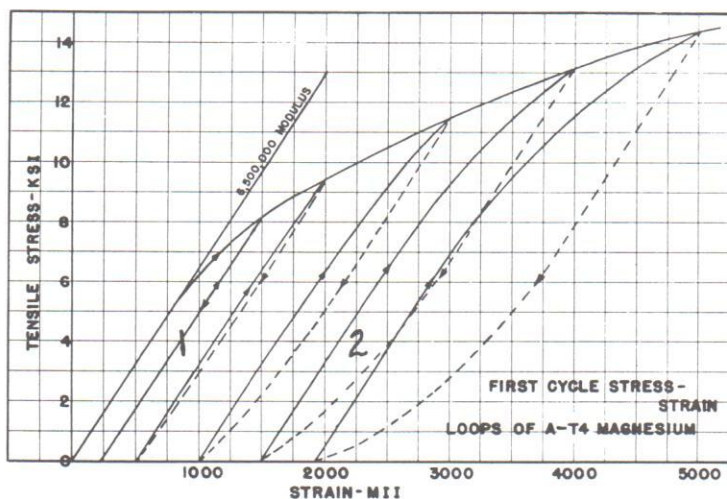
(a) Loop 1: $\sigma_1 = 1$ ksi, $\sigma_2 = 5$ ksi.

$$\text{Ans: } W'_1 = -30.21 \text{ ft} \cdot \text{lb}_f.$$

(b) Loop 2: $\epsilon_1 = 2000 \mu\text{in/in}$, $\epsilon_2 = 2500 \mu\text{in/in}$.

$$\text{Ans: } W'_2 = -119.7 \text{ ft} \cdot \text{lb}_f.$$

Since W'_1 and W'_2 are negative, work was done on the cylinder.



First cycle uniaxial tensile stress-strain curves for Dowmetal A-T4 magnesium alloy. Loops 1 and 2 are labeled. MII = microinches/inch. (From M.H. Polzin, 1951, Fig. 9 with modifications. Reprinted by permission of the Society for Experimental Mechanics, Inc., Bethel, CT.)