

# Preface

Thermodynamics is not the oldest of sciences. Mechanics can make that claim. Thermodynamics is a product of some of the greatest scientific minds of the 19th and 20th centuries. But it is sufficiently established that most authors of new textbooks in thermodynamics find it necessary to justify their writing of yet another textbook. I find this an unnecessary exercise because of the centrality of thermodynamics as a science in physics, chemistry, biology, and medicine. I do acknowledge, however, that instruction in thermodynamics often leaves the student in a confused state. My attempt in this book is to present thermodynamics in as simple and as unified a form as possible.

As teachers we identify the failures of our own teachers and attempt to correct them. Although I personally acknowledge with a deep gratitude the appreciation for thermodynamics that I found as an undergraduate, I also realize that my teachers did not convey to me the sweeping grandeur of thermodynamics. Specifically the simplicity and the power that James Clerk Maxwell found in the methods of Gibbs were not part of my undergraduate experience. Unfortunately some modern authors also seem to miss this central theme, choosing instead to introduce the thermodynamic potentials as only useful functions at various points in the development.

I introduce the combination of the first and second laws and then the complete set of the potentials appears in chapter four. The remainder of the text is then built on the potentials. Before discussing modern laboratory measurements, for example, I show that the fundamental quantities sought in the laboratory are those which are required for determining the potentials.

The question of how to present our microscopic understanding of matter in a thermodynamics course confronts the author of any text. Presently the subjects of thermodynamics and statistical mechanics are a seamless whole [cf. [154, 155]]. I believe that we should try to convey that to our students without recourse to probability arguments. And so I have elected to present statistical mechanics as an integral part of the text. I begin with a chapter that takes the reader as far as we can go with simple models of molecules. Then I present ensemble theory as succinctly and simply as I am able, with the seamless connection to thermodynamics. Because of the

modern work in Bose Einstein Condensation and in astrophysics, I then added a chapter on quantum statistical mechanics.

Because of its importance in modern applications I have chosen to treat irreversibility and the ideas of Ilya Prigogine. This provides a logical transition into the application of thermodynamics to chemical reactions. And irreversibility is at the center of all of biophysics.

I have used irreversibility as a step to considerations of stability and then to chemical equilibrium, solutions, and the equilibrium of heterogeneous systems. As a physicist I have also looked at chemical reaction rates and transition state theory. TST is a very interesting branch of theoretical physics. I encourage any physicist considering this text to not disregard this chapter.

This text is intended to be used as an introduction to modern thermodynamics and statistical mechanics. I believe it has the depth that can be appreciated without the extreme length to which many textbooks have gone. Consistent with this I have limited the exercises at the end of chapters. The exercises I have used are not intended to teach methods of solution nor are they intended as drill. Some are even intended as vehicles for investigation.

I suspect that my interests as a physicist will be apparent. My original training as an engineer, however, has led me to believe that applications only follow from understanding. Thermodynamics is subtle.

As an author I owe deep debts of gratitude to many that I can never hope to repay. I encountered the beauty and subtlety of thermodynamics first from Jerzy R. Moszynski. I was privileged then to work with David Mintzer and Marvin B. Lewis, from whom I gained an understanding of statistical mechanics and kinetic theory. I am also very grateful to generations of students who have helped this text emerge from my efforts to introduce them to thermodynamics. In an evaluation one student remarked that you have to work to hang on, but if you do the ride is worth it. I am also grateful to those who have been personally involved in the writing of this book. My wife, Betty Jane, has provided patience, understanding, and support, without which this book never would have been written. And Thomas von Foerster read and commended on the first drafts of almost all of the chapters. His critique and insistence have been invaluable.

Goshen, IN  
August, 2008

*Carl Helrich*

# Chapter 2

## Formulation

*A theory is more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression which classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.*

Albert Einstein

### 2.1 Introduction

Einstein's conviction, expressed in the quotation above, is based in part on the care with which thermodynamics is constructed as a science. In our discussions in the preceding chapter we have not required precise definitions of terms and concepts. Indeed these may have hindered the discussion. As we begin to formulate the science in such a way that we can have confidence in the results of our formulation, we must, however, define terms and concepts carefully.

In his chapter we will introduce thermodynamic systems, states and processes. We will also present the basic principles or laws of thermodynamics. These laws govern the behavior of material substances in transformations associated with thermodynamic processes. The goal of this chapter is to present a brief, but sufficiently complete discussion that will result in the basic formulation of the thermodynamics of closed systems in terms of a single mathematical statement.

### 2.2 Systems and Properties

#### 2.2.1 Systems

In a thermodynamic analysis we always consider a system. The system is a particular amount of a substance contained within definable boundaries. The substance

we may consider can be quite general. In most of what we do this will be matter composed of particles, i.e. atoms and/or molecules. However, we do not exclude systems containing radiation (photons). The substance need not be a single element or compound. And we shall treat substances containing particles that may undergo chemical reactions. And the substance or substances present may be in any phase or phases: solid, liquid or gas.

### **2.2.2 Boundaries**

Boundaries separate the system under consideration from the immediate surroundings. These may be real material boundaries or imagined. We define the properties of the boundary so that the interaction between the system and the surroundings is specified in terms necessary for the analysis. Whether physically real or imaginary, the system boundary is real as far as the system properties are concerned.

Generally systems may be either impervious or open to the exchange of substances (matter) with the surroundings. Systems which are impervious to the exchange of matter with the surroundings are closed systems. Otherwise the system is open. In either case the system boundary may be fixed, such as a solid wall, or movable, such as a piston.

If we are interested in the heating of a solid block, for example, the boundary is most conveniently considered to be the outer surface of the block itself. The boundary is then closed and movable. The boundary is closed because the block neither gains nor loses mass. The boundary is movable because the block expands on heating. The boundary is physically real because the surface of the block is a real physical surface.

The analysis of a uniformly flowing fluid provides an example of an open system with a fixed boundary. A portion of the system boundary may be determined by a curved surface defined by the streamlines of the flowing fluid. The streamlines are defined by the velocity of the flow and there is no macroscopic flow across streamlines. In some circumstances we may be able to identify a real solid boundary that is parallel to the streamlines, such as for flow through a pipe or a nozzle. We complete the system by closing the ends of our system by open, imaginary surfaces at the ends, through which the fluid flows.

System boundaries are also classified according to whether or not they are permeable to heat. An adiabatic boundary is impermeable to the flow of heat. Heat may flow across a diathermal boundary. A system placed within a rigid adiabatic enclosure is then completely isolated from its surroundings. Work may be done on a system in a rigid adiabatic boundary in a Joule experiment using paddle wheels to stir the fluid. But an adiabatically enclosed system can do work on the surroundings only if the boundary is movable. If two systems are separated by a diathermal boundary, heat will flow from one system to the other until the temperatures of the two systems are equal. In a state of equilibrium, then, the temperatures of two systems separated by a diathermal boundary are the same.

System boundaries may then be open or closed, rigid or movable, and adiabatic or diathermal.

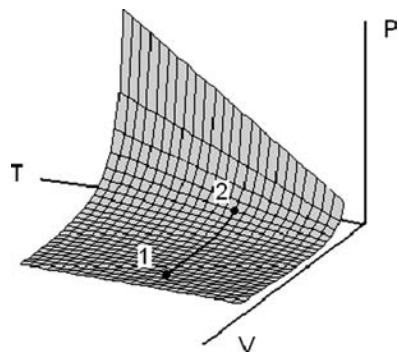
### 2.2.3 Properties and States

Pressure,  $P$ , volume,  $V$ , and temperature,  $T$ , are examples of thermodynamic properties of a system. The thermodynamic state of a system is determined if the thermodynamic properties of the system are known. We consider, for example, a system containing a certain amount of gas in a cylinder with a piston that is free to move vertically. The volume of the system is known from the position of the piston and the pressure of the system is determined by the weight of the piston and the weight of any mass that may be added to the piston. If the cylinder is diathermal the temperature of the system is the temperature of the room. The values of  $P$ ,  $V$ , and  $T$  specify the thermodynamic state, or simply state of the system. We implicitly assume that  $P$  and  $T$  are uniform throughout the system so that we can speak of a single pressure and temperature of the system.

If there is no change in the state of the system with time we define the state as one of thermodynamic equilibrium.

### 2.2.4 Surfaces and States

Experiment shows that for any substance the three properties  $P$ ,  $V$ , and  $T$  are not independent, but are related in a particular way that depends upon the identity of the substance. Specification of any two of these properties determines the third. For example, the pressure,  $P$ , is a function of the temperature,  $T$ , and the volume,  $V$ . The function  $P = P(T, V)$  is then a surface in  $(P, V, T)$  space. An example is shown in Fig. 2.1. Each point on the surface in Fig. 2.1 is the representation of a thermodynamic state.



**Fig. 2.1** The  $(P, V, T)$  surface. This is the graphical representation of the thermal equation of state. Figures 2.4, 2.6, 2.7, and 2.13 in reference [145] are beautiful representations of such surfaces

The relationship  $P = P(V, T)$  is called the *thermal equation of state* for the substance and the surface in Fig. 2.1, is referred to as a  $(P, V, T)$  surface. A substance such as a gas, for which there are two independent thermodynamic properties, is called simple. Most substances of interest in applications are of this type. So we shall tentatively assume simple substances, or systems, in this text.

In general the thermal equation of state will not be known as an algebraic function. In these circumstances we must rely on tabulated data. The thermodynamic properties for many substances of interest have been tabulated (cf. [87] and [88]). The National Institute of Standards and Technology also has a database, *NIST Reference Fluid Thermodynamics and Transport Properties - REFPROP* [102], which can be purchased and used on a personal computer. *REFPROP Version 8* (April, 2007) has been used as a source of data extensively in this text.

### 2.2.5 Quasistatic Processes

The most efficient heat engines are those for which the changes in the thermodynamic state of the working substance are slow enough that the system may be considered to remain in an equilibrium state. In such processes there are very small differences between internal and external forces and an infinitesimal change in the external force will result in a reversal of the process. These processes are called quasistatic or reversible. An example is the process  $1 \rightarrow 2$  in Fig. 2.1. In this process the state of the substance lies on the line drawn on the surface at each instant. Each of the states on this line are equilibrium states. The process then carries the substance (in the system) from one equilibrium state to another.

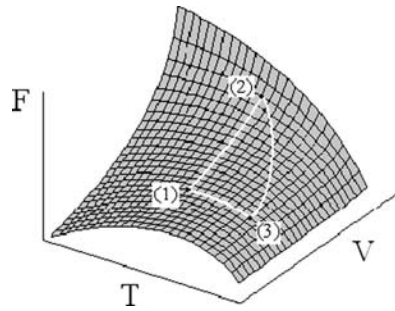
Real processes of interest are seldom if ever quasistatic. It is often possible, however, ignore the details and base the analysis on changes in thermodynamic properties.

For situations in which the variations in thermodynamic conditions are small over dimensions of interest or slow over measurement times, an assumption of local equilibrium may be made. That is, we may consider that thermodynamic equilibrium exists for small volumes and over short times resulting in an ability to apply the results of equilibrium thermodynamics to the situation. We may then speak meaningfully about thermodynamic variables as having values which depend on position and on the time within a system.

### 2.2.6 Properties and Processes

A thermodynamic property may be any general quantity that has a unique value for each thermodynamic state of a substance. That is a thermodynamic property a unique function of the thermodynamic state of the system. Two such functions are the internal energy and the entropy.

**Fig. 2.2** A graphical representation of a thermodynamic property  $F(T, V)$ . Separate processes to change the thermodynamic state from (1) to (2) are shown



Changes in the value of a thermodynamic properties in a process are independent of the details of the process. The function  $F(T, V)$  plotted in Fig. 2.2 is an example of a thermodynamic property. The value of the property  $F$  is the height of the surface above the  $(T, V)$  plane. We consider a quasistatic change in the thermodynamic state from (1) to (2). We may change the thermodynamic state of the system by holding the temperature constant and varying the volume. This is the direct path from (1) to (2) in Fig. 2.2. The change in  $F$  in this process is  $\Delta F = F(2) - F(1)$  and is the difference in the heights of the surface  $F(T, V)$  above the  $(T, V)$  plane at points (1) and (2). We may also hold the volume constant while we take the system first through a quasistatic change in the thermodynamic state from (1) to (3) and then follow this by a general quasistatic change in state from (3) to (2) during which both  $T$  and  $V$  vary. The resulting change in the value of  $F$  in the second process  $(1) \rightarrow (3) \rightarrow (2)$ , is also  $\Delta F = F(2) - F(1)$  and simply equal to the difference in the heights of the surface  $F(T, V)$  above the  $(T, V)$  plane at points (1) and (2).

Calculations of the changes in values of thermodynamic properties may then be carried out choosing any process whatsoever carrying the system from the initial to the final thermodynamic state.

## 2.3 Properties and the Laws

*Die Energie der Welt ist Konstant. Die Entropie der Welt strebt einem Maximum zu.* (The energy of the universe is constant. The entropy of the universe tends to a maximum)

Rudolf Clausius, 1865.

Three thermodynamic properties are defined by the laws of thermodynamics. These are temperature, internal energy and entropy. In our historical outline of the preceding chapter we presented the background behind the first and second laws. These provide a basic understanding of heat and the motive power of heat. The first law defines the internal energy of a substance and the second law defines the entropy. Integral to the discussion of these laws was the concept of temperature, which we treated as an intuitive concept. It was not until the 20th century that we recognized that the definition of temperature requires another law. Because this should logically precede the first and second laws it is called the *zeroth law*.

### 2.3.1 Temperature

The sense of “hotter” or “colder” is physiological. Items in a room are all essentially at the same temperature, although a table may feel colder than a book. The physiological sensation is based on a rate of heat transfer upon touch rather than temperature. The thermodynamic definition of temperature is based on observable behavior of systems independent of human physiology.

We noted above that two systems in equilibrium with a diathermal boundary between them will have the same temperature. For example if a test tube containing oil is immersed in a beaker of water both the oil and the water will have the same temperature when a state of thermodynamic equilibrium is reached. To verify the equality in temperatures we must perform a measurement. And to measure the temperature of the water or of the oil we require a third system: a thermometer. Introducing this necessary third system brings us beyond the statement of equality of temperatures of the first two systems. We must logically make a statement about the third system.

In 1931, while reviewing a thermodynamics text by the great Indian astrophysicist, Megh Nad Saha,<sup>1</sup> Ralph H. Fowler<sup>2</sup> observed that for consistency the statement that [150]

*If systems A and B are both in equilibrium across a diathermal boundary with system C, then systems A and B will be in equilibrium with one another if separated by a diathermal wall.*

should be included in the formulation of thermodynamics.

System *C* is our thermometer. We only need to arrange the system *C* in some contrived fashion so that we can easily determine its thermodynamic equilibrium state when it is in contact with the systems *A* and *B*. This statement then resolves our logical problem and serves to make the definition of an empirical (experimentally determined) temperature possible. This is the zeroth law.

We have been using *T* to designate temperatures. At this stage in our discussion *T* is an empirical temperature. With the zeroth law we have a more robust and definitive statement of the meaning of temperature than our previous intuitive concept. But this is not yet what we shall identify as a thermodynamic temperature. The thermodynamic or absolute temperature is a quantity, which will result from the second law.

An example of an empirical temperature scale is that determined by a mercury in glass thermometer. Our third system here is a glass capillary tube which is partially filled with mercury under vacuum so that only mercury vapor exists above the liquid mercury. If we neglect the vapor pressure of the mercury we have a system at a constant pressure (equal to zero).

---

<sup>1</sup> Meghnad Saha FRS (1893–1956) was an Indian astrophysicist. He is best known for the Saha equation, which gives the density of electrons in an ionized gas.

<sup>2</sup> Sir Ralph Howard Fowler OBE FRS (1889–1944) was a British physicist and astronomer.



The expansion of the liquid mercury with changes in temperature is much greater than that of the glass so we may safely assume that only the length of the mercury column varies with temperature. We have then contrived our system so that the length of the mercury column is the only property we need to measure in order to determine the temperature. The length is the thermometric property. The scale we choose as a measure of the length of the mercury column is arbitrary. For simplicity we may choose the scale to be linear. This requires two constants to fix the scale, or the specification of two standard temperatures. If these are taken to be separated by 100 degrees we have a centigrade scale. If the standard temperatures are also the ice and steam point of water the scale is the Celsius scale.

To specify our empirical temperature scale we must describe the system (mercury in a glass capillary tube filled under vacuum), our thermometric property (length of mercury column), our scale (linear), and the fixed points (ice and steam).

In the appendix we present the ideal gas temperature scale as an empirical scale which requires only a single fixed point and for which there is an absolute zero fixed by the universal properties of gases as their pressures approach zero. This scale is identical with the thermodynamic scale.

In the appendix we find that the ideal gas has a thermal equation of state

$$P(V, T) = nR \frac{T}{V}$$

in which  $n$  is the number of mols and  $R$  is a universal constant known as the (universal) gas constant. This defines a fictitious substance that will, nevertheless, prove very useful.

### 2.3.2 Internal Energy

A definition of internal energy as a thermodynamic property comes from the first law. Thomson pointed out that Joule's experiments identified this property and provided a method for its measurement. We have chosen to formulate the first law, following Clausius, as an energy conservation theorem. Nevertheless our formulation reduces to that of Joule and Thomson for the relationship between work and internal energy. We, therefore, still require a definition of thermodynamic work.

#### Thermodynamic Work

Joule's original experiment provides an unambiguous definition of thermodynamic work. The work done by or on a thermodynamic system may always be used to raise or lower a body of mass  $m$  a distance  $\pm h$  in the earth's gravitational field. This work is  $\pm mgh$ , where  $g$  is the acceleration due to the gravitational field of the earth. Thermodynamic work is then defined in unambiguous mechanical terms as

**Definition 2.3.1.** *Thermodynamic work is defined as any interaction of the thermodynamic system with the surroundings that can be reduced to the raising or lowering of a material body in the gravitational field.*

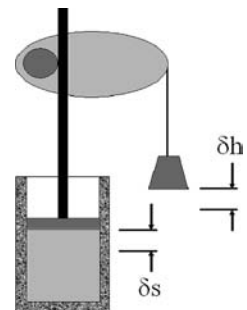
The intended use to which we put the work done may not be to raise or lower a material body. The question of whether or not thermodynamic work has been done in a process is based, however, on whether or not we can imagine an arrangement of pulleys and gears that can reduce the final effect to raising or lowering of a material body.

This definition of thermodynamic work allows us to obtain an expression for the quasistatic (reversible) work done on or by a closed system. In a closed system it is only possible to perform quasistatic thermodynamic work by moving a boundary such as a piston. Figure 2.3 illustrates how this work can be reduced to the lowering of a material body in the gravitational field. The cylinder contains a gas and the force of the weight is transmitted to the piston by a cam arrangement. For practical purposes we may consider that the suspended mass is on a balance pan. If we remove a small amount of mass from the pan the piston and the suspended mass will both move upward. The motion of the body through the distance  $\delta h$  corresponds to a motion of the piston through a distance  $\delta s$ . In this process the internal force on the piston is a product of the system pressure,  $P$ , and the piston area,  $A$ . As the piston moves a distance  $\delta s$  the work done by the system on the surroundings is  $PA\delta s = P\delta V$ , where  $dV (= A\delta s)$  is the differential change in the system volume. If there is no friction in the cam system or the piston this is equal to  $mg\delta h$  in which  $m$  is the suspended mass remaining. Then, for a very small step in a quasistatic process occurring in a closed system, the work done by the system on the surroundings is

$$\delta W_{\text{rev}} = PdV. \quad (2.1)$$

We have taken the limit  $\delta V \rightarrow dV$  as the weight removed becomes infinitesimal and have written  $\delta W_{\text{rev}}$  for the reversible quasistatic work done.

The dependence of  $P$  on  $V$  is determined by the process involved. Therefore the infinitesimal quasistatic work done  $\delta W_{\text{rev}}$  is process dependent, as we pointed out in Chap. 1.



**Fig. 2.3** Thermodynamic work is done by the closed system as the piston moves raising or lowering the mass

If  $dV > 0$  work is done by the system on the surroundings and the mass is raised. If  $dV < 0$  work is done by the surroundings on the system and the mass is lowered.

### 2.3.2.1 Closed Systems

For an infinitesimal, quasistatic (reversible) process occurring in a closed system we write the first law in (1.2) as

$$\delta Q_{\text{rev}} = dU + PdV. \quad (2.2)$$

The differential change in the internal energy is then given by

$$dU = \delta Q_{\text{rev}} - PdV. \quad (2.3)$$

Both terms on the right hand side of (2.3) are process dependent. But their difference is the differential of a thermodynamic property and is not process dependent.

The internal energy is defined by a differential expression provided by the first law. That is, only differences in internal energy are defined. The internal energy in integrated form is then only determined to within a constant, which may be chosen to be zero at an arbitrary point. This choice of a zero for the internal energy implies nothing about the actual value of the energy of a system of atoms or molecules, which never vanishes (see Sects. 10.3.3 and 10.4.2)

### 2.3.2.2 Open Systems

*General.* Matter may cross the boundary of a system as a result of thermodynamic forces on the boundary or, as in many engineering applications, because of entrance and exit ports in the system. In an open system there will be contributions to the energy associated with the transport of matter across the system boundary. The identity of these contributions depends on the system, the process taking place and the system design. We shall combine these additional contributions to the system energy in an infinitesimal process to form the term  $d\Phi$ . In engineering applications open systems are often used to produce work other than the  $PdV$  work associated with the motion of the system boundary. This work is traditionally called “shaft work” and is designated as  $\delta W_s$ . The first law for an open system is then

$$dU = \delta Q + d\Phi - \delta W_s - PdV. \quad (2.4)$$

In this equation  $\delta Q$  is a general heat transfer, which may include irreversible as well as reversible contributions.

*Engineering Applications.* In engineering applications matter enters and leaves the system through a number of ports such as steam lines. In this case the term  $d\Phi$  contains contributions from energy transported by the matter and the work done on or by the system in transporting the matter. Work done in the transport of matter is considered to be an energy term. We shall designate the ports by superscripts  $i$  and the number of mols of substance  $\lambda$  entering or leaving the  $i$ th port in an infinitesimal process as  $d_e n_\lambda^{(i)}$ .

At the  $i$ th port the component  $\lambda$  has a specific (molar) energy determined by the conditions at the  $i$ th port,

$$e_\lambda^{(i)} = \epsilon_\lambda^{(i)} + u_\lambda^{(i)}. \quad (2.5)$$

Here  $\epsilon_\lambda^{(i)}$  contains all forms of energy besides the (thermodynamic) internal energy, which we designate as  $u_\lambda^{(i)}$ .

The work required to transport matter into or out of port  $i$  is equal to the product of the pressure force at the port,  $P_i$ , and the volume occupied by the matter transported,  $d_e n_\lambda^{(i)}$ , which is  $V_i = v_\lambda^{(i)} d_e n_\lambda^{(i)}$ . This results in an increase of the energy of the system if the matter is transported into the system and a decrease if the matter is transported out of the system.

The term  $d\Phi$  resulting from the transport of matter is then

$$\begin{aligned} d\Phi &= \left( \epsilon_\lambda^{(i)} + u_\lambda^{(i)} + P_i v_\lambda^{(i)} \right) d_e n_\lambda^{(i)} \\ &= \left( \epsilon_\lambda^{(i)} + h_\lambda^{(i)} \right) d_e n_\lambda^{(i)}. \end{aligned} \quad (2.6)$$

Here

$$h_\lambda^{(i)} = u_\lambda^{(i)} + P_i v_\lambda^{(i)} \quad (2.7)$$

is the specific (molar) enthalpy<sup>3</sup> of the component  $\lambda$  at the port  $i$ .

In engineering applications the system of interest generally possesses energies in addition to the thermodynamic internal energy. We, therefore, write  $d\mathcal{E}$  in place of  $dU$ . The general conservation of energy in (2.4) for open engineering systems then takes the form

$$d\mathcal{E} = \delta Q - \delta W_s + \sum_i \epsilon_i d n_i + \sum_i h_i d n_i. \quad (2.8)$$

In (2.8) any  $PdV$  work is involved in transport of matter.

**Specific Heats.** From (2.7) we have the enthalpy of a single component system as

$$H = nh = U + PV. \quad (2.9)$$

---

<sup>3</sup> The origin of the term enthalpy is with the Dutch physicist Heike Kamerlingh Onnes who derived its meaning from the Greek word "en-thal'-pos" ( $\epsilon\nu\theta\alpha\lambda\pi\omicron\zeta$ ). Accent is on the second syllable.

The first law for a closed system can then be written as either (2.2) or as

$$\delta Q_{\text{rev}} = dH - VdP. \quad (2.10)$$

Since the heat transferred will produce a change in the system temperature at either constant volume or constant pressure we realize that  $dU$  in (2.2) and  $dH$  in (2.10) must both be proportional to  $dT$  and that  $U$  and  $H$  must be functions of the temperature  $T$ . Because (2.2) already contains  $dV$  we are led to assume that  $U$  will depend on the temperature  $T$  and the volume  $V$ . And because (2.10) already contains  $dP$  we similarly assume that  $H$  depends on  $T$  and  $P$ . We may then measure the temperature increase  $dT$  in the system resulting from an amount of heat transferred quasistatically  $\delta Q_{\text{rev}}$ . The quantity  $\delta Q_{\text{rev}}/dT$  is called the *heat capacity*.

The concept of the heat capacity of a substance predates the work of Joule and, therefore, our present understanding of heat transfer as the transport of energy. The unit of the *calorie* was defined as the amount of heat required to raise the temperature of one gram of water by  $1^\circ\text{C}$  when the pressure is 1 atm (101.325 kPa). The properties of water are temperature dependent and the amount of heat required to raise the temperature of one gram of water by  $1^\circ\text{C}$  depends upon the temperature at which the measurement is made. The  $20^\circ\text{C}$  calorie, or  $20^\circ\text{ cal}$  (4.1816 J) was the amount of heat required to raise one gram of water from  $19.5$  to  $20.5^\circ\text{C}$  at 1 atm pressure and the  $15^\circ\text{ cal}$  (4.1855 J) was the amount of heat required to raise the temperature from  $14.5$  to  $15.5^\circ\text{C}$  at a pressure of 1 atm. These values defined the heat capacity of water as a function of temperature [50].

With our present understanding of thermodynamics we realize that the measurement required in this definition of the calorie is given in (2.10) with  $dP = 0$ . That is

$$\text{heat capacity} = \frac{\delta Q_{\text{rev}}]_P}{dT} = \frac{1}{n} \left( \frac{\partial H(T, P)}{\partial T} \right)_P, \quad (2.11)$$

in which  $n$  is the number of mols of the substance present in the system. Because  $H = H(T, P)$  is a property of the substance, the quantity defined in (2.11) is also a property of the substance. The term defined in (2.11) is no longer called the heat capacity, but the (molar) *specific heat at constant pressure*,  $C_P(T, P)$ , defined by

$$C_P(T, P) \equiv \frac{1}{n} \left( \frac{\partial H(T, P)}{\partial T} \right)_P. \quad (2.12)$$

Similarly (2.2) provides a definition of a (molar) *specific heat at constant volume*,  $C_V(T, V)$ , defined as

$$C_V \equiv \frac{1}{n} \left( \frac{\partial U(T, V)}{\partial T} \right)_V. \quad (2.13)$$

Because  $U = U(T, V)$  is a property of the substance (it is a thermodynamic potential) the specific heat at constant volume is a property of the substance.

**Perpetual Motion.** Let us consider an isolated, adiabatically enclosed system consisting of interconnected subsystems, which we designate with the subscript  $\sigma$ . This system can be made to go through a cyclic process by performing work on the system and allowing work to be done by the system. That is we may arrange a system of pulleys and gears so that weights are raised and lowered. If the system undergoes a cyclic process all subsystems must also undergo cyclic processes. The internal energy change of the system, and of each subsystem taken separately must be zero if the process is cyclic. The first law requires that the net work done by each subsystem is then equal to the net heat input to the subsystem in the cycle,

$$W_\sigma = Q_\sigma. \quad (2.14)$$

But the system is adiabatic. So there is no heat transferred to the system in any process. The net heat transferred to the system is the algebraic sum of the heats transferred to all the subsystems. Then

$$\sum W_\sigma = \sum Q_\sigma = 0, \quad (2.15)$$

Therefore no net work can be obtained from a cyclic process occurring in a closed adiabatic system. In order to obtain work from a cycle there must be a transfer of heat to the cycle.

A thermodynamic cycle that produces a net work without the input of heat is called a perpetual motion machine of the first kind. The status of the first law of thermodynamics is such that we can deny the possibility of a perpetual motion machine of the first kind with absolute confidence.

### 2.3.3 Entropy

The thermodynamic property introduced by the second law is the entropy. We already introduced the entropy in terms of reversible heat transfer and the (not yet defined) thermodynamic temperature in Sect. 1.3.2 (see (1.3)). There we also referred to the introduction of the entropy and its relation to irreversibility as one of the great steps in theoretical physics. We should not then expect that a simple mathematical definition and a single paragraph will provide all we require.

In this section we shall outline the steps that carry us from the original experimental evidence, showing that there are limitations on what can be done, to a succinct mathematical expression of those limitations. The difficulty in the enterprise is in the fact that we are dealing with limitations rather than positive statements. In our presentation here we shall lift out the principle steps in the development, leaving details to the appendix.

Because the limitations of the second law are formulated in terms of thermodynamic cycles our mathematical development must be first carried out in those terms. We will later be able to cast the entropy in statistical terms (see Sect. 9.7.1).

**The Verbal Statements.** There are two fundamental statements of the second law. These are due, respectively, to Clausius, and to Thomson (Lord Kelvin). They are

- I. Clausius *No cyclic process exists which has as its sole effect the transference of heat from a body at a temperature  $\Theta_2$  to a body at a temperature  $\Theta_1$  if  $\Theta_1 > \Theta_2$ .*
- II. Kelvin *No cyclic process exists which has as its sole effect the transference of heat from a single body and the complete conversion of that into an equivalent amount of thermodynamic work.*

We can show that these statements are logically equivalent by demonstrating that a violation of one implies a violation of the other. Traditionally the argument is based on Carnot's most efficient engine.

**Carnot's Theorem.** The ideas leading to the formulation of the second law are Carnot's. So we formally introduce the entropy  $S$  and the thermodynamic temperature  $T$  through what is now known as Carnot's theorem.

**Theorem 2.3.1.** (*Carnot's Theorem*) *There exist two functions of state,  $S$  and  $T$ , where  $T$  is a positive function of the empirical temperature alone, such that in any infinitesimal quasistatic change of state in a system the heat transfer is  $\delta Q_{rev} = T dS$ .*

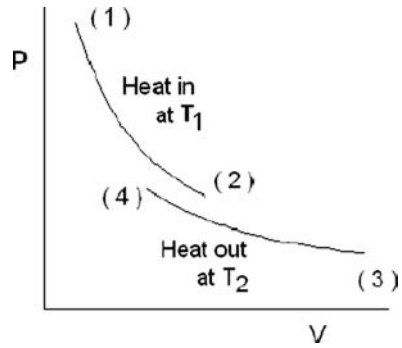
To make this definition of the entropy complete we must add the statement that the entropy increases in any irreversible process. Proof of this is based on the Clausius inequality, which is the final goal of this section.

**Carnot Cycle.** Carnot realized that any difference in temperature can be used to obtain work, and that the most efficient cycle possible will operate quasistatically (see Sect. 1.2). Any transfer of heat must then be carried out isothermally and quasistatically.

To see how this can be done we consider the system in Fig. 2.3 but assume that the cylinder is not insulated. Removal of a very small mass from the balance pan will produce an expansion of the gas at constant temperature. This results in work done by the system and heat transfer to the system. Heat can be transferred from the system isothermally by adding weights.

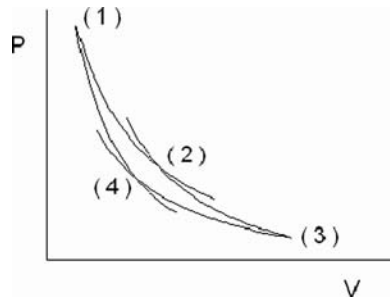
In the cycle we must transfer heat to the system at a high temperature and from the system at a low temperature. Plotting pressure against volume we have the situation shown in Fig. 2.4. We consider that the cycle begins at point (1). Heat is taken in along the isotherm at temperature  $T_1$  and the system volume expands until the system reaches the state (2). Heat is exhausted along the isotherm at  $T_2$  from (3) to (4) with a decrease in volume.

**Fig. 2.4** Reversible isothermal heat transfer to and from a Cycle. Heat is transferred to the system at  $T_1$  and exhausted from the system at  $T_2$



Because a cycle must take the system back to the starting point (1), the two isotherms in Fig. 2.4 must be connected by two other processes. Since heat must only be transferred isothermally, these connecting processes cannot transfer any heat. They must be adiabatic. The completed cycle is that shown in Fig. 2.5.

**Fig. 2.5** The Carnot cycle composed of two isotherms and two adiabats



The cycle shown in Fig. 2.5 is then the most efficient that can possibly be constructed to operate between the two heat reservoirs at temperatures  $T_1$  and  $T_2$ . In this cycle

- 1–2 Heat is transferred into the system isothermally while work is done by the system.
- 2–3 Work is done by the system during adiabatic expansion.
- 3–4 Heat is transferred from the system isothermally while work is done on the system.
- 4–1 Work is done on the system by adiabatic compression.

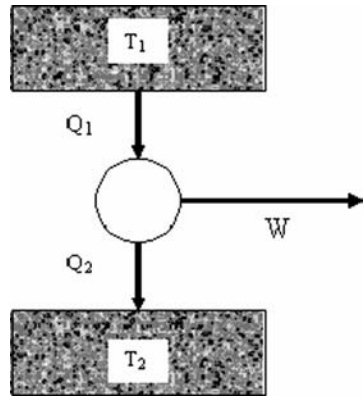
This is the Carnot Cycle.

We may also represent the Carnot cycle symbolically as shown in Fig. 2.6. The heat transferred to the cycle at  $T_1$  is  $Q_1$  and that transferred from the cycle at  $T_2$  is  $Q_2$ . The work done is  $W$ . From the first law,  $W = Q_1 - Q_2$ .

The Carnot cycle is an ideal cycle. Each of the isothermal and adiabatic steps alone can be carried out using a cylinder with a piston. But the combination becomes



**Fig. 2.6** The Carnot cycle represented symbolically. The *blocks* indicated by  $T_1$  and  $T_2$  are the high and low temperature reservoirs.  $Q_1$  and  $Q_2$  are heats transferred.  $W$  is the work done in the cycle



impractical. We would have to insulate the cylinder during parts of the cycle and then remove the insulation for others. The Carnot cycle is primarily a thinking piece for the proof of Carnot's theorem.

We can, however, approximate the Carnot cycle in practice. Water boils producing steam at a constant temperature and the steam condenses again to water at a single lower temperature. And because steam and water pass through them very rapidly, turbines and pumps are approximately adiabatic. A steam power plant then has the characteristics of a Carnot cycle.

**Carnot Efficiency.** From Fig. 2.6 the thermodynamic efficiency of the Carnot cycle  $\eta_C$  is

$$\eta_C = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}. \quad (2.16)$$

In the appendix we provide an outline of the classical development of the second law. There we show that the ratio of the heats transferred to and from a Carnot cycle is equal to a ratio of two functions each of which depends solely on the temperature of one of the reservoirs. That is

$$\frac{Q_2}{Q_1} = \frac{\tau(\text{temperature } 2)}{\tau(\text{temperature } 1)}, \quad (2.17)$$

where  $\tau$  is a function of the (empirical) temperature alone. These functions of temperature can never be zero, since the rejected heat  $Q_2$  can never vanish by the second law. Thomson (Lord Kelvin) suggested that we use the relationship in (2.17) to define a temperature, which is the *positive function of the empirical temperature alone* referred to in Carnot's theorem. That is  $\tau = T$ . This is the thermodynamic or absolute (Kelvin) temperature.

The efficiency of the Carnot cycle is independent of the working substance in the cylinder (see Appendix). Therefore the thermodynamic temperature requires no reference to any substance used in its measurement. Its definition depends solely on the first and second laws of thermodynamics.

In the remainder of this text we will always understand  $T$  to be the thermodynamic temperature.

With the thermodynamic temperatures  $T_1$  and  $T_2$ , (2.17) becomes

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}, \quad (2.18)$$

and Carnot efficiency is

$$\eta_C = \frac{T_1 - T_2}{T_1}. \quad (2.19)$$

**Clausius Inequality.** We may use the fact that the entropy must increase in a spontaneous process occurring in an isolated system to obtain an integral inequality that elegantly expresses this property. We consider that an isolated system is in a thermodynamic state (1) and that a spontaneous process occurs within the system after which the system is in state (2). We then devise a set of reversible processes that will bring the system back to state (1). The change in the system entropy during the reversible processes bringing it from (2) back to (1) is

$$S_1 - S_2 = \int_2^1 \frac{\delta Q_{\text{rev}}}{T}.$$

Since the original spontaneous process produced a positive entropy change we know that  $S_2 > S_1$ . Therefore

$$\int_2^1 \frac{\delta Q_{\text{rev}}}{T} < 0. \quad (2.20)$$

We now consider that the spontaneous process resulting in the initial state change from (1)  $\rightarrow$  (2) becomes infinitesimal, but does not vanish. In the limit the states (1) and (2) will then become indistinguishable and the integral in (2.20) becomes an integral around a cycle. That is we have

$$\oint_{\text{cycle}} \frac{\delta Q}{T} < 0 \quad (2.21)$$

if an irreversible process occurs anywhere in the cycle. Because the integral around the cycle now incorporates an infinitesimal irreversible process we designate the infinitesimal heat transfer as  $\delta Q$  rather than  $\delta Q_{\text{rev}}$ . If no irreversible process occurs the integral vanishes because  $\delta Q_{\text{rev}}/T$  is the differential of the property  $S$ . In general, then, the second law requires that

$$\oint \frac{\delta Q}{T} \leq 0. \quad (2.22)$$

This is the Clausius inequality. It is a complete mathematical statement of the second law, provide we append the statement that the equality only holds in the absence of any irreversible process in the cycle. In that case  $\delta Q \rightarrow \delta Q_{\text{rev}}$  and the definition of the entropy as

$$dS = \delta Q_{\text{rev}}/T \quad (2.23)$$

emerges from the fact that the integral of  $dS$  around a cycle vanishes.

## 2.4 Combining the Laws

The first and second laws appear to express different aspects of what, with Carnot, we may call the motive power of heat. But there must be a unifying principle. We are speaking of the interaction of matter with energy. The fact that we are employing this in the production of useful work is incidental to the understanding we seek.

The unifying principle appears in (2.23). Although the term  $\delta Q_{\text{rev}}$  is path dependent and not itself a differential of a function, the entropy, whose differential is defined in (2.23), is a thermodynamic property. That is we convert the path dependent (problematic) term  $\delta Q_{\text{rev}}$  to the differential of a property if we multiply it by  $1/T$ . If we use the form of  $\delta Q_{\text{rev}}$  provided by the first law, we have

$$dS = \frac{1}{T}dU + \frac{P}{T}dV. \quad (2.24)$$

as a differential for the entropy of a closed system. This is equivalent to equating the two definitions of the quantity  $\delta Q_{\text{rev}}$  appearing in (2.3) and (2.23).

$$TdS = dU + PdV. \quad (2.25)$$

This was first done by Gibbs [57]. And (2.25) is known as the *Gibbs equation*. The Gibbs equation is the foundational mathematical statement of thermodynamics.

In an address entitled *The Problems of Mathematics* delivered to the *Second International Congress of Mathematicians* in Paris in 1900, David Hilbert<sup>4</sup> defined 23 unsolved problems confronting mathematicians at the beginning of the new (20th) century. Number six among these was to axiomatize all of physics. Because the physics that came out of the 20th century was not the physics Hilbert envisaged, physics will not be axiomatized. Nevertheless, in 1909 Constantin Carathéodory<sup>5</sup>

<sup>4</sup> David Hilbert (1862–1943) was a German mathematician. Hilbert was professor of mathematics at Göttingen.

<sup>5</sup> Constantin Carathéodory (1873–1950) was born in Berlin of Greek parents, grew up in Brussels, and obtained his Ph.D. at Göttingen. The work referred to here was "Investigations on the Foundations of Thermodynamics" (Untersuchungen über die Grundlagen der Thermodynamik, Math. Ann., 67 p. 355–386 (1909))

was able to establish rigorously that  $dS$  in (2.25) is an exact differential. Herbert Callen<sup>6</sup> referred to the analysis of Carathéodory as a tour de force of delicate and formal logic [20]. The importance of this contribution cannot be overstated because of the centrality of thermodynamics as a science.<sup>7</sup>

The laws of thermodynamics are the three discussed in this section and the third law, or Nernst hypothesis, which we shall consider in a later chapter. The zeroth law is a logical statement which clarifies the concept of temperature, but contributes nothing to the structure of thermodynamics. The third law, as we shall see, provides understanding of the behavior of thermodynamic properties as the thermodynamic temperature approaches absolute zero. The third law opened an entire new area of investigation of the behavior of matter at low temperatures and provides absolute values for certain thermodynamic properties critical in physical chemistry. But the third law has no direct consequence for the motive power of heat or for the behavior of matter at moderate or high temperatures. The basis of much of our study and application of thermodynamics is then a combination of the first and second laws. And this combination is presented succinctly, and beautifully, in the Gibbs equation.

The Gibbs equation is a relationship that must hold among infinitesimal changes in entropy, internal energy, and volume of any physical substance. That is it defines a surface in a space in which the axes are  $U$ ,  $V$ , and  $S$ . Thermodynamics requires that all possible states accessible to the system must lie on this surface. The geometrical form of this fundamental thermodynamic surface must then hold the key to our understanding of the behavior of matter in its interaction with energy. This is the key to an understanding of thermodynamics.

## 2.5 Summary

In this chapter we have presented the basic concepts required for a study of thermodynamics. These included systems, thermodynamic properties and states, and the principles or laws of thermodynamics. Each of these concepts is important for our understanding of the power, beauty, and the limitations of the science.

All of thermodynamics is based on studies of systems. When we speak of processes and cycles we must bear in mind that these occur in systems with well defined boundaries. The laws of thermodynamics will provide relations among thermodynamic properties. In any application of thermodynamics, however, it is critical that we understand the identity of the system involved.

The formulation of thermodynamics must include a discussion of the laws. We have, therefore, included a brief, but basically complete discussion of the first three laws of thermodynamics. In this we have chosen to make the laws understandable. We have, however, deviated from an approach based only on experimental evidence.

---

<sup>6</sup> Herbert B. Callen (1919–1993) was professor of physics at the University of Pennsylvania. He is author of *Thermodynamics and an Introduction to Thermostatistics*, one of the most widely cited books in physics.

<sup>7</sup> We have provided an outline of Carathéodory's principle in the appendix.

The claim that energy (or the total mass-energy of relativity) is conserved is presently accepted based on our experience of more than a century since the first law was formulated. But this was not the case for Clausius. We have followed Clausius' path to accepting conservation of energy as the fundamental principle. An alternative, philosophically more positivist approach would be based solely on experiment. The final mathematical statement of the first law is unchanged. In the positivist approach heat transfer is, however, a derived concept defined in terms of the measurable thermodynamic work.

The second law can also be treated in a more positivist framework. Although satisfying, the development in this framework is involved and is not transparent. We have, therefore, elected to present the concepts of the second law without proof based on either direct experimental evidence or on rigorous mathematics. The standard, classical development of the second law is presented in the appendix.

## Exercises

**2.1.** You want to study heating of a moving, nontoxic liquid. You mount a section of pipe on the laboratory table, connect one end of the pipe to a cold source of the liquid, and the other end you exhaust into a large reservoir. Around the pipe you wrap heating wire and insulation. You can measure the power supplied to the heater.

What is your system if you are interested in the temperature rise of the liquid? Classify the system.

**2.2.** Fuel and oxidant are sprayed into a rocket combustion chamber and burning takes place. Hot gases, which may still be reacting, leave the chamber and enter the nozzle. Assume that the combustion chamber is approximately spherical.

(a) You are interested in the combustion process. Where will you draw your system? Define the boundaries. Classify the system.

(b) If you are interested in the mixing process for the fuel and oxidant, where is the system boundary? Classify the system.

**2.3.** You want to measure the thermal conductivity of a fluid. To do this you propose to place a platinum wire in the fluid and use the wire as a heat source. An electrical current in the wire will produce the heat and this will be transferred by conduction into the fluid. The wire will then itself be used as a thermometer so that the temperature field around the wire will not be affected by the introduction of a separate measuring device. In the experiment the temperature of the wire will be measured as a function of time.

It is known that the resistance of a platinum wire varies linearly with the temperature. Describe the empirical temperature scale you intend to set up for your experiment.

- 2.4.** You are designing a steam power plant and have decided that it helps your thought pattern to return to Clausius' way of picturing heat transfer and work done. Use arrows for heat and work. In your plant you will have a boiler operating at a temperature of  $T_1$ . You may assume that the steam coming out of the boiler has that temperature. You have cooling coils which you can locate either in cooling towers or in the local river. Call the low temperature of the cooling coils  $T_2$ .
- A turbine does the work, which is then used to drive a generator. The best you can hope for is an efficiency  $\eta = W/Q_{in} = (T_1 - T_2)/T_1$ .
- Redraw the Clausius cycle indicating clearly the location of the boiler, cooling coils, heat engine.
  - The temperature of the river is  $\Delta T$  (degrees) lower than the cooling coils. You want to increase efficiency. You can either raise the boiler temperature by  $\Delta T$  or opt out for the river over the towers. Which do you choose to obtain the greatest increase in efficiency?
- 2.5.** The ideal gas is a simple model to use in calculations. We obtained equations for  $\delta Q_{rev}$  in terms of both  $dU$  and  $dH$  for the ideal gas we also will find that the specific heats are constants. Defining  $\gamma = C_P/C_V$ , and using the equations for  $dU$  and  $dH$  in terms of  $\delta Q_{rev}$  show that for the ideal gas  $PV^\gamma = \text{constant}$  in an adiabatic reversible (isentropic) process.
- 2.6.** Show that the empirical ideal gas temperature  $T_g$ , which we can take to be defined by the ideal gas equation of state obtained from a gas thermometer (see Appendix) as  $P = RT_g/V$ , is identical to the thermodynamic temperature, which is defined in terms of the heats transferred to and from a Carnot engine  $Q_{in}/Q_{out} = T_{high}/T_{low}$ .
- 2.7.** Assume that the atmosphere is isothermal. If  $\rho$  is the air density the mass of a volume  $dV = Adh$ , where  $A = \text{area}$  and  $dh = \text{height}$ , of air is  $dm = \rho Adh$ . The weight of this mass of air is supported by the difference in pressures  $dP = P_2 - P_1$  between the bottom of  $dV$  and the top (a distance  $dh$ ). Find the variation in pressure with altitude of an isothermal atmosphere if air is an ideal gas.
- 2.8.** A helium balloon, which is a sphere of radius  $r$ , rises in an isothermal atmosphere. Assume also that the difference in pressure of the helium inside the balloon and that of the atmosphere outside is given by  $P_{He} - P_a = \alpha/r$ . This is known as the Laplace equation for the excess pressure inside a bubble, where the constant  $\alpha$  is proportional to the surface tension. The temperature of the helium will be that of the atmosphere. Assume helium is an ideal gas. What is the relationship between the balloon radius and the height to which the balloon rises?
- 2.9.** A rubber bag contains  $m$  kilograms of sand at a temperature  $T_0$ . The sand has a specific heat of

$$C_V = (\alpha T + \beta) \text{ kJ kg}^{-1},$$

where  $\alpha$  and  $\beta$  are constants. Assume that the rubber bag is adiabatic to a reasonable approximation. The bag of sand is dropped from a height of  $h$  m onto the laboratory floor, which is hard epoxy. Assume no energy in any form is transferred to this hard floor. The bag also does not bounce.

What is the rise in temperature of the sand?

- 2.10.** Consider a volume contained in an adiabatic boundary. The volume consists of two separate, but identical parts with an adiabatic boundary between them. One compartment contains  $n_A$  mols of gas  $A$  at temperature  $T_A$  and pressure  $P_A$ . The other contains  $n_B$  mols of gas  $B$  at temperature  $T_B > T_A$  and pressure  $P_B$ . Let the specific heat of the gas  $A$  be  $(3/2)R$  and of the gas  $B$  be  $(5/2)R$ . The two compartments are connected through a valve (a stopcock). You can open the valve and the gases will flow freely between compartments. Assume the gases to be ideal so that the molecules behave completely independently of one another.

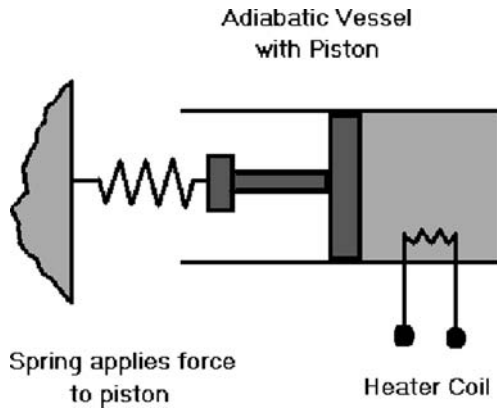
What is the entropy produced in the process?

- 2.11.** Consider a gas contained in a cylinder with a movable piston. The gas is taken sequentially through constant pressure and constant volume processes. The gas is first in state we shall call  $A$ . By placing a particular mass on the top of the piston the pressure is maintained at a pressure  $P_2$  while the volume is increased from  $V_1 \rightarrow V_2$  to point  $B$ . Then the piston is clamped in place and the pressure is decreased to a value of  $P_1$  to point  $C$ . The next step is like the first in that a mass on the piston keeps the pressure constant as the volume is decreased to  $V_1$  at point  $D$ . The final step goes back to  $A$  with the piston clamped in place.

Plot the cycle on the  $(P, V)$  – plane.

- Which steps require doing work on the system? In which steps is work done by the system? In which steps is no work done at all?
  - Is there net work done on or by the system? What is the net work?
  - In which processes is heat flow into the system? In which is heat flow out of the system?
  - What is the total change in internal energy in the cycle?
  - Recalling Carnot's idea that heat engines should work on a cycle, what you have is a cycle that could be used as a heat engine. The engine may be difficult to build in practice. But the cycle is there. Do you need additional information to compute the efficiency of this engine?
- 2.12.** Find the work done by an ideal gas in (a) an isothermal process and (b) an isentropic process. Which is greater between the same initial states and the same final volumes? Indicate this graphically by drawing both processes on a  $(P, V)$  plane and showing the work done in each process.
- 2.13.** In the system shown here a  $n$  mols of a gas are contained in an adiabatic vessel. The vessel has an internal heating coil which supplies an amount of heat,  $Q$ , to the system. The gas temperature increases and the spring is compressed. You make three measurements on the system: the power supplied to the coil

$P$  and the time taken  $\Delta t$  (i.e. you measure the total energy supplied by the battery to the coil) and the compression,  $x$ , of the spring. Find the increase in temperature of the gas. Assume the gas to be ideal.



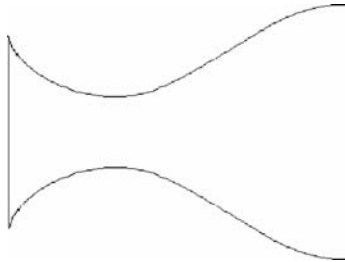
- 2.14.** Consider the isothermal heat transfer steps in a Carnot engine. The engine is in contact with large isothermal reservoirs during these steps. The working substance you may assume is an ideal gas.
- What is the change in entropy for each reservoir?
  - What is the change in entropy for the gas during a cycle in terms of any change in thermodynamic state variables? In terms of the heat transferred?
  - What is the total change in entropy of the gas system and the surroundings?
- 2.15.** You have a thermodynamic cycle which, when plotted in the  $(T, S)$  plane is a rectangle. The cycle is from  $A$  (in the upper right hand corner)  $\rightarrow B \rightarrow C \rightarrow D \rightarrow A$ .
- Show that the work done in this cycle is equal to the area enclosed in the  $(T, S)$  diagram.
  - What is the heat transferred to or from the system in each step of the cycle?
  - What is the entropy change in the cycle?
  - What is the efficiency of this cycle?

Do you recognize the cycle?

- 2.16.** A nozzle converts thermal energy into kinetic energy. The combustion chamber is to the left of the nozzle shown here. Designate the conditions in the combustion chamber by subscript 1. The thermodynamic state of the gas is known and the velocity is essentially zero. Designate the conditions of the gas at the exit by the subscript 2. The velocity at the exit is  $\mathcal{V}$ .

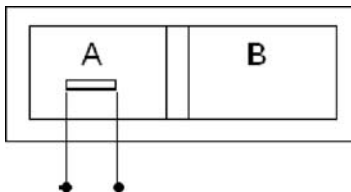


- (a) Find  $\mathcal{V}$  in terms of the temperature difference and the mass flow rate.
- (b) What has the nozzle done in energy terms.
- (c) explain the concept of thrust of the rocket engine.



- 2.17.**(a) A  $100\Omega$  resistor is immersed in an oil bath. The oil bath remains at a constant temperature of  $27^\circ\text{C}$ . A current of  $100\text{mA}$  flows in the resistor for  $50\text{S}$ . Find the entropy change of the resistor and of the oil bath. At the beginning at at the end of the experiment the temperature of the resistor is that of the oil bath.
- (b) Instead of placing the resistor in the above problem in an oil bath assume it is thermally insulated. That is you enclose it in an adiabatic boundary. The resistor has a mass of  $5\text{ g}$  and the material from which it is made has a specific heat at constant pressure of  $850\text{Jkg}^{-1}\text{K}^{-1}$ . The other parameters for the experiment are the same. What is the change in entropy of the resistor? You may assume that the experiment is conducted under constant pressure. Assume also that the resistor volume change is negligible during the experiment.

- 2.18.** The vessel shown here is insulated (adiabatic) and the two compartments are separated by a frictionless adiabatic piston. In compartment *A* is a heater with electrical connections to the outside. The total volume of the vessel is  $V$ . Initially the two compartments *A* and *B* are filled with equal amounts of the same monatomic ideal gas at the same temperature ( $T_0$ ) and pressure ( $P_0$ ). The heater is turned on and the piston moves to the right very slowly until the volume of the right compartment is  $V_B < V/2$ . What is the heat supplied?



- 2.19.** A metal cylinder is divided into two compartments by a metal disk welded to the walls. One compartment contains a gas under pressure. The other is empty. The empty compartment is  $9$  tenths of the total volume. Initially the gas in the

compartment behind the disk has temperature  $T_1$ , pressure  $P_1$ , and volume  $V_1$ . The disk is punctured remotely and the gas expands to fill the vessel. The final and initial temperatures are the same (that of the room).

- (a) The process is irreversible. The entropy will increase. What is the increase in entropy?
  - (b) We realize that an increase in entropy means we have lost the ability to do work. We decide to put in a movable (frictionless) piston with a rod passing through the evacuated part of the vessel to the outside where we can use the work done. We move the piston slowly so the process is isothermal and quasistatic. How much work can we get?
- 2.20.** A reversible engine gains heat from a single reservoir at 400 K and exchanges heat, at two points in the cycle, to reservoirs at 300 K and at 200 K. During a number of cycles the engine absorbs 1200 J of heat from the reservoir at 400 K and performs 200 J of thermodynamic work.
- (a) find the quantities of heat exchanged with the reservoirs at 300 K and at 200 K and decide whether the engine absorbs or exhausts heat at each reservoir.
  - (b) Find the change in entropy of each reservoir.
  - (c) What is the change in entropy of the engine plus surroundings?
- 2.21.** You have two identical metal blocks at different temperatures  $T_1$  and  $T_2$  with  $T_1 > T_2$ . The block mass of each block is  $m$  and the specific heat of the metal at constant pressure is  $C_p$ . You may assume that there is no change in volume of the blocks. The temperature in the laboratory is  $T_0 = (T_1 + T_2)/2$ . The temperatures of the two blocks may be made equal in a number of ways. You consider three ways.
- (a) Bring the blocks into contact with one another.
  - (b) Place the blocks in a large constant temperature oil bath ( $T_0$ ). The oil bath has mass  $M_{\text{bath}}$  and specific heat  $C_{p,\text{bath}}$ .
  - (c) Use the two blocks as reservoirs for a Carnot cycle and run the cycle until the temperatures are the same.

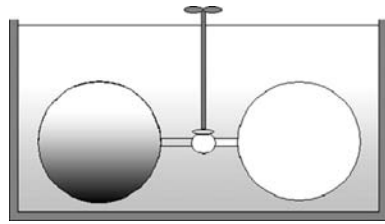
What is the final temperature and the entropy produced in each method? You should find a greater increase in entropy when the bath is used as an intermediary. Think about this.

How does the final temperature in (c) compare to the laboratory temperature? Comment on this.

- 2.22.** An experiment to measure the dependence of the internal energy of a gas on volume was first conducted in 1807 by Joseph-Louis Gay-Lussac (1778–1850) and later reproduced by Joule. The experimental apparatus is shown in Fig. 2.7. A glass vessel with two parts separated by a stopcock was immersed in a water bath. One part of the vessel contains the gas of interest and the other is initially evacuated. In the experiment the stopcock was opened and the gas flowed freely into the evacuated part of the vessel. A thermometer in

the water bath measures the change in the water temperature resulting from the free expansion of the gas.

**Fig. 2.7** Gay-Lussac apparatus

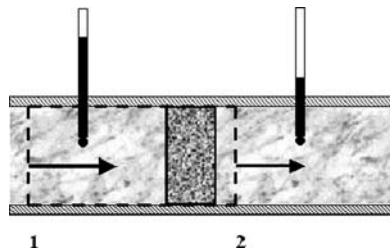


Analyze the experiment based on the first law and relate the temperature measurement to  $(\partial U/\partial V)_T$ . Do you make any assumptions about the apparatus?

- 2.23.** In a classic experiment designed by Joule and Thomson to measure the dependence of enthalpy on pressure a gas was forced through a porous plug of cotton wool [84, 85]. The core of the experimental apparatus of Joule and Thomson is shown in Fig. 2.8. The pipe was made of beechwood and insulated. Thermometers were located on both sides of the cotton wool. Pressure on each side of the wool plug were maintained by cylindrical reservoirs with weighted covers [[4], p. 138]. The gas flowed very slowly through the cotton wool under pressure. The gas velocities on either side of the plug could then be neglected. The dashed line is a system boundary enclosing a constant amount of air.

Using the first law for open systems, show that in this experiment the thermal enthalpy is a constant.

In the experiment pressures and temperatures were measured on both sides of the wool plug. So the experiment measured  $(\partial T/\partial P)_H$ , which has become known as the Joule-Thomson, or simply Joule coefficient  $\mu_J = (\partial T/\partial P)_H$ . How to extract  $(\partial H/\partial P)_T$  from  $\mu_J$  is a mathematical question that will be investigated in Chap. 3.



**Fig. 2.8** The Joule-Thomson apparatus

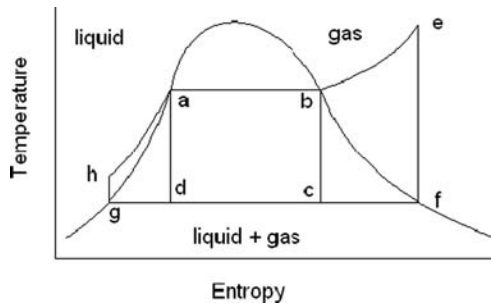
- 2.24. Throttling.** Rather than the wool plug of the Joule-Thomson experiment consider a pipe with a constriction, such as a partially opened valve or a long and narrow capillary. The process is known as throttling and has industrial applications [[89], p. 248]. Analyze flow through a throttling valve using the

first law. Assume that the incoming fluid is moving slowly. If you neglect the kinetic energy compared to the thermal enthalpy change, you should have the result that throttling is an isenthalpic process.

**2.25.** You are impressed that the most efficient cycle must transfer heat isothermally and that the other legs of the cycle must be isentropic. The cycle plotted on  $(S, T)$  coordinates is a rectangle.

You know that the isentropic assumption may be made when a fluid flows rapidly, because then the heat transfer per mol is small. Turbines do this very well. So you can use a turbine to obtain work isentropically. You also know that water boils and condenses at constant temperatures if the pressures are held constant.

In Fig. 2.9 we have plotted the idea in  $(S, T)$  coordinates for water. The saturation line and the phases of water are indicated.



**Fig. 2.9** Carnot and Rankine cycles plotted in the  $(S, T)$  plane of water. The saturation line is shown

The Carnot cycle is  $a \rightarrow b \rightarrow c \rightarrow d$ . The leg  $b \rightarrow c$  is the turbine, and you propose to pump the partially condensed liquid from  $d \rightarrow a$  to enter the boiler. The difficulty becomes clear after some thought. So you elect to heat the steam to a higher temperature before entrance to the turbine and you allow the condensation to run to completion. The result is the cycle  $a \rightarrow b \rightarrow e \rightarrow f \rightarrow c \rightarrow d \rightarrow g \rightarrow h$ . The small vertical leg  $g \rightarrow h$  is the liquid pump, which is also isentropic.

- (a) Explain the problems that led to super heating and full condensation.
- (b) In which legs are work done and is this by or on the system?
- (c) Draw the cycle on a sheet of paper and indicate heat into the cycle and heat exhausted.
- (d) What represents the work done?
- (e) Where are boiling and condensation?

This cycle is actually the Rankine cycle and forms the basis of power production.

**2.26.** Conduct a first law analysis of the boiler and the turbine in for the cycle in Exercise 2.25. Use the Eq. (2.8) written for a time dependent process, i.e.

$$d\mathcal{E}/dt = \dot{Q} - \dot{W}_s + \sum_i e_i dn_i/dt + \sum_i h_i dn_i/dt.$$

Here all terms are rate terms.  $\dot{Q}$  and  $\dot{W}_s$  are rate of heat transfer and rate at which work is done. For steady state processes  $d\mathcal{E}/dt = 0$  because the total energy of the system does not change in time. The terms  $dn_i/dt$  are mass flow rates at the ports with flow in positive.

- 2.27.** Consider running the cycle in Exercise 2.25 in reverse. That is we replace the turbine with a compressor, condense the fluid at the high temperature and boil it at the low temperature. We no longer use water for this. Describe what you have.

