CHAPTER 3

THERMODYNAMICS OF DILUTE GASES

3.1 INTRODUCTION

The motion of a compressible fluid is directly affected by its thermodynamic state which is itself a consequence of the motion. For this reason, the powerful principles of thermodynamics embodied in the first and second law are a central part of the theory of compressible flow. Thermodynamics derives its power from the fact that the change in the state of a fluid is independent of the actual physical process by which the change is achieved. This enables the first and second laws to be combined to produce the famous Gibbs equation which is stated exclusively in terms of perfect differentials of the type that we studied in Chapter1. The importance of this point cannot be overstated and the reduction of problems to integrable perfect differential form will be a recurring theme throughout the course.

3.2 THERMODYNAMICS

Thermodynamics is the science that deals with the laws that govern the relationship between temperature and energy, the conversion of energy from one form to another especially heat, the direction of heat flow, and the degree to which the energy of a system is available to do useful work.

Temperature and the zeroth law

In his classic textbook *"The Theory of Heat"* (SpringerVerlag 1967) Richard Becker begins with the following description of temperature.

"The concept of temperature is basic in thermodynamics. It originates from our sensations, warm and cold. The most salient physical property of temperature is its tendency to equalize. Two bodies in contact (thermal contact!) will eventually have the same temperature, independent of their physical properties and the special kind of contact. Just this property is used to bring a substance to a given temperature, namely, by surrounding it with a heat bath. Then, by definition, substance and heat bath have the same temperature. To measure the temperature one can employ any physical property which changes continuously and reproducibly with temperature such as volume, pressure, electrical resistivity, and many others. The temperature scale is fixed by convention."

In this description, Becker postulates an incomplete law of equilibrium whereby two systems placed in thermal contact will spontaneously change until the temperature of each system is the same. This is sometimes called the zeroth law of thermodynamics. James Clerk Maxwell (1831-1879), the famous British physicist, who published his own text entitled *"Theory of Heat"* in 1870, expressed the zeroth law as follows: When each of two systems is equal in temperature to a third, the first two systems are equal in temperature to each other.

A key concept implicit in the zeroth law is that the temperature characterizes the state of the system at any moment in time and is independent of the path used to bring the system to that state. Such a property of the system is called a *variable of state*.

The first law

During the latter part of the nineteenth century heat was finally recognized to be a form of energy. The first law of thermodynamics is essentially a statement of this equivalence. The first law is based on the observation that the internal energy E of an isolated system is conserved. An isolated system is one with no interaction with its surroundings. The internal energy is comprised of the total kinetic, rotational and vibrational energy of the atoms and molecules contained in the system. Chemical bond and nuclear binding energies must also be included if the system is undergoing a chemical or nuclear reaction.

The value of the internal energy can only be changed if the system ceases to be isolated. In this case E can change by the transfer of mass to or from the system, by the transfer of heat, and by work done on or by the system. For an adiabatic, ($\delta Q = 0$), constant mass, system, $dE = -\delta W$.

By convention, δQ is positive if heat is added to the system and negative if heat is removed. The work, δW is taken to be positive if work is done *by* the system *on* the surroundings and negative if work is done *on* the system *by* the surroundings.

Because energy cannot be created or destroyed the amount of heat transferred into a system must equal the increase in internal energy of the system plus the work done by the system. For a nonadiabatic system of constant mass,

$$\delta Q = dE + \delta W \qquad (3.1)$$

This statement, which is equivalent to a law of conservation of energy, is known as the first law of thermodynamics.

In equation (3.1) it is extremely important to distinguish between a small change in internal energy which is a state variable and therefore is expressed as a perfect differential d, and small amounts of heat added or work done that do not characterize the system per se but rather a particular interaction of the system with its surroundings. To avoid confusion, the latter small changes are denoted by a δ.

The internal energy of a system is determined by its temperature and volume. Any change in the internal energy of the system is equal to the difference between its initial and final values regardless of the path followed by the system between the two states.

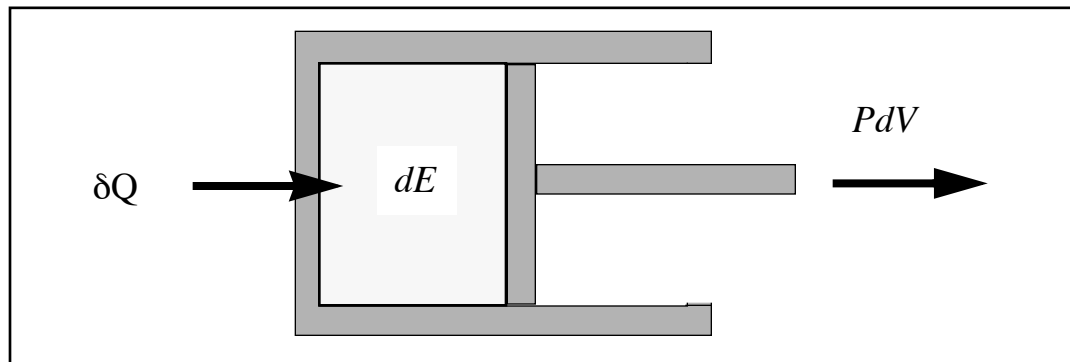Consider the piston cylinder combination shown below.

*Figure 3.1   Exchange of heat and work for a system enclosed in
a cylinder with a movable piston.*

The cylinder contains some *homogeneous* material with a fixed chemical composition. An infinitesimal amount of heat, δQ is added to the system causing an infinitesimal change in internal energy and an infinitesimal amount of work δW to be done. The differential work done by the system on the surroundings is the conventional mechanical work done by a force acting over a distance and can be expressed in terms of the state variables pressure and volume. Thus

$$\delta W \ = \ Fdx \ = \ (F/A)d(Ax) \ = \ PdV \tag{3.2}$$

where A is the cross sectional area of the piston and F is the force by the material inside the cylinder on the piston. The first law of thermodynamics now takes the form.

$$\delta Q = dE + PdV \tag{3.3}$$

We will be dealing with open flows where the system is an infinitesimal fluid element. In this context it is convenient to work in terms of intensive variables by dividing through by the mass contained in the cylinder. The first law is then,

$$\delta q = de + Pdv \tag{3.4}$$

where δq is the heat exchanged per unit mass, e is the internal energy per unit mass and $v = 1/\rho$ is the volume per unit mass. As noted above, the δ symbol is used to denote that the differential 1-form on the right-hand-side of (3.4) is not a perfect differential and in this form the first law is not particularly useful.

The first law (3.4) is only useful if we can determine an equation of state for the substance contained in the cylinder. The equation of state is a functional relationship between the internal energy per unit mass, specific volume and pressure, $P(e, v)$. For a general substance an accurate equation of state is not a particularly easy relationship to come by and so most applications tend to focus on approximations based on some sort of idealization. One of the simplest and most important cases is the equation of state for an ideal gas which is an excellent approximation for real gases over a wide range of conditions. We will study ideal gases shortly but first let's see how the existence of an equation of state gives us a complete theory for the equilibrium states of the material contained in the cylinder shown in Figure 3.1.

The second law

Assuming an equation of state can be defined, the first law becomes,

$$\delta q = de + P(e, v)dv \tag{3.5}$$

According to Pfaff's theorem, discussed in Chapter 1, the differential form on the right-hand-side of (3.5) must have an integrating factor which we write as $1/T(e, v)$. Multiplying the first law by the integrating factor turns it into a perfect differential.

$$\frac{\delta q}{T(e, v)} = \frac{de}{T(e, v)} + \frac{P(e, v)}{T(e, v)}dv = ds(e, v) \tag{3.6}$$

In effect, once one accepts the first law (3.5) and the existence of an equation of state, $P(e, v)$, *then the existence of two new variables of state is implied*. By Pfaff's theorem there exists an integrating factor which we take to be the inverse

of the temperature postulated in the zeroth law, and there is an associated integral called the entropy (per unit mass), $s(e, v)$. In essence, the second law implies the existence of stable states of equilibrium of a thermodynamic system.

The final result is the famous Gibbs equation, usually written

$$\boxed{Tds \ = \ de + Pdv}. \tag{3.7}$$

This fundamental equation is the starting point for virtually all applications of thermodynamics. Gibbs equation describes states that are in local thermodynamic equilibrium i.e., states that can be reached through a sequence of reversible steps.

Since (3.6) is a perfect differential, the partial derivatives of the entropy are

$$\left.\frac{\partial s}{\partial e}\right|_{v \ = \ constant} \ = \ \frac{1}{T(e, v)} \qquad \left.\frac{\partial s}{\partial v}\right|_{e \ = \ constant} \ = \ \frac{P(e, v)}{T(e, v)}. \tag{3.8}$$

The cross derivatives of the entropy are equal and so one can state that for *any* homogeneous material

$$\frac{\partial^2 s}{\partial e \partial v} \ = \ \frac{\partial}{\partial v}\left(\frac{1}{T(e, v)}\right) \ = \ \frac{\partial}{\partial e}\left(\frac{P(e, v)}{T(e, v)}\right) \tag{3.9}$$

Note that the integrating factor (the inverse of the temperature) is not uniquely defined. In particular, there can be an arbitrary, constant scale factor since a constant times ds is still a perfect differential. This enables a temperature scale to be defined so that the integrating factor can be identified with the measured temperature of the system.

3.3 THE CARNOT CYCLE

Using the Second Law one can show that heat and work, though each is a form of energy, are not equivalent. All work can be converted to heat but not all heat can be converted to work. The Carnot cycle involving heat interaction at constant temperature is the most efficient thermodynamic cycle and can be used to illustrate

this point. Consider the piston cylinder combination containing a fixed mass of a working fluid shown below and the sequence of piston strokes representing the four basic states in the Carnot cycle.
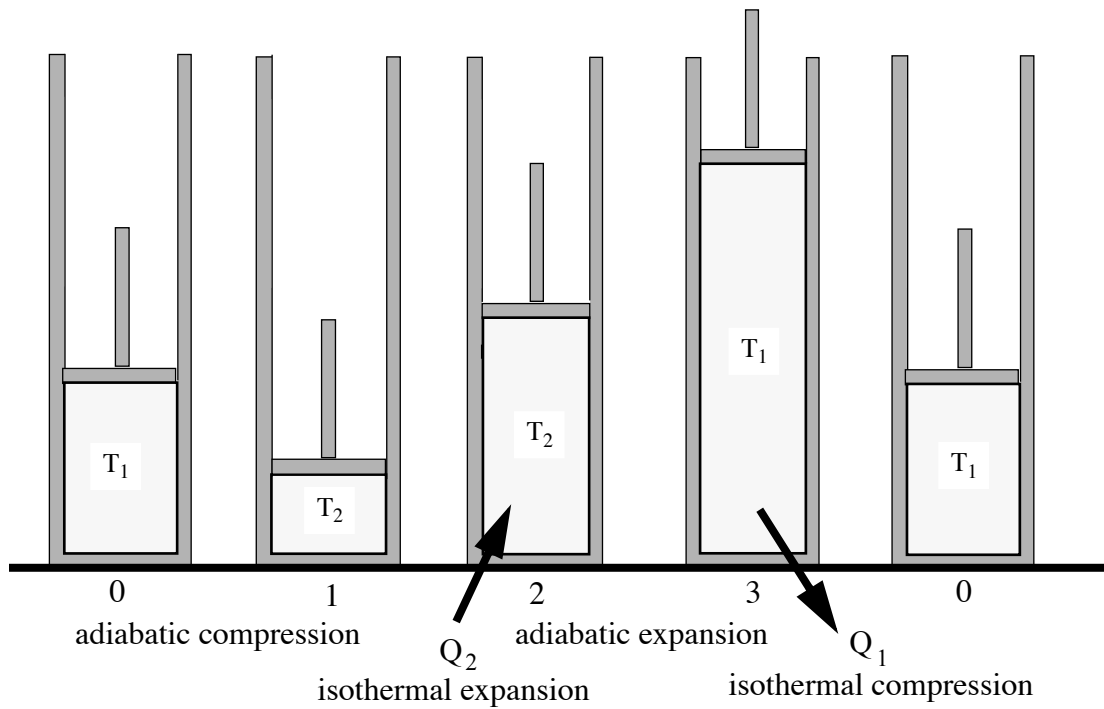

Figure 3.2   The Carnot Cycle heat engine

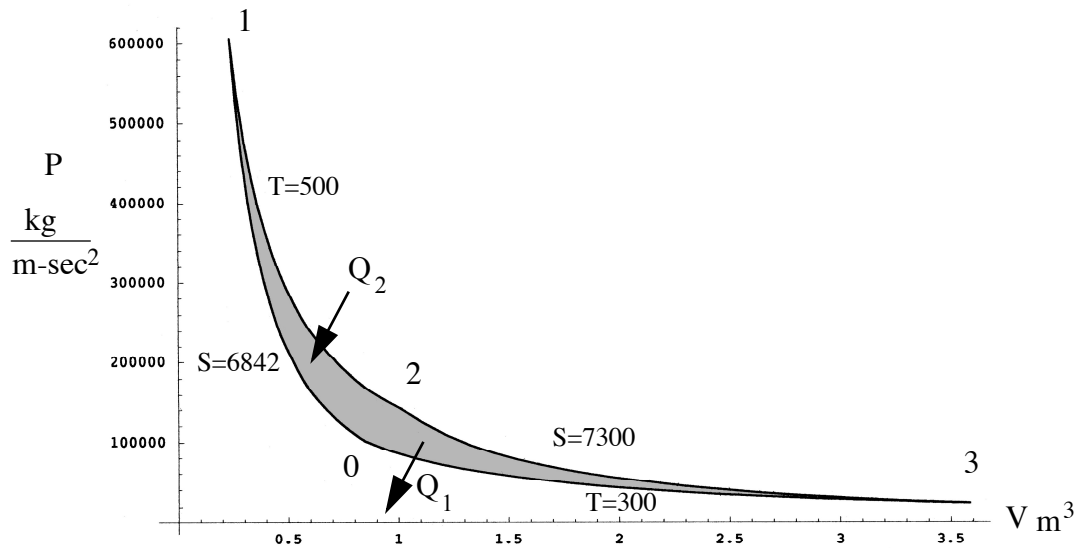In the ideal Carnot cycle the adiabatic compression and expansion strokes are carried out isentropically.

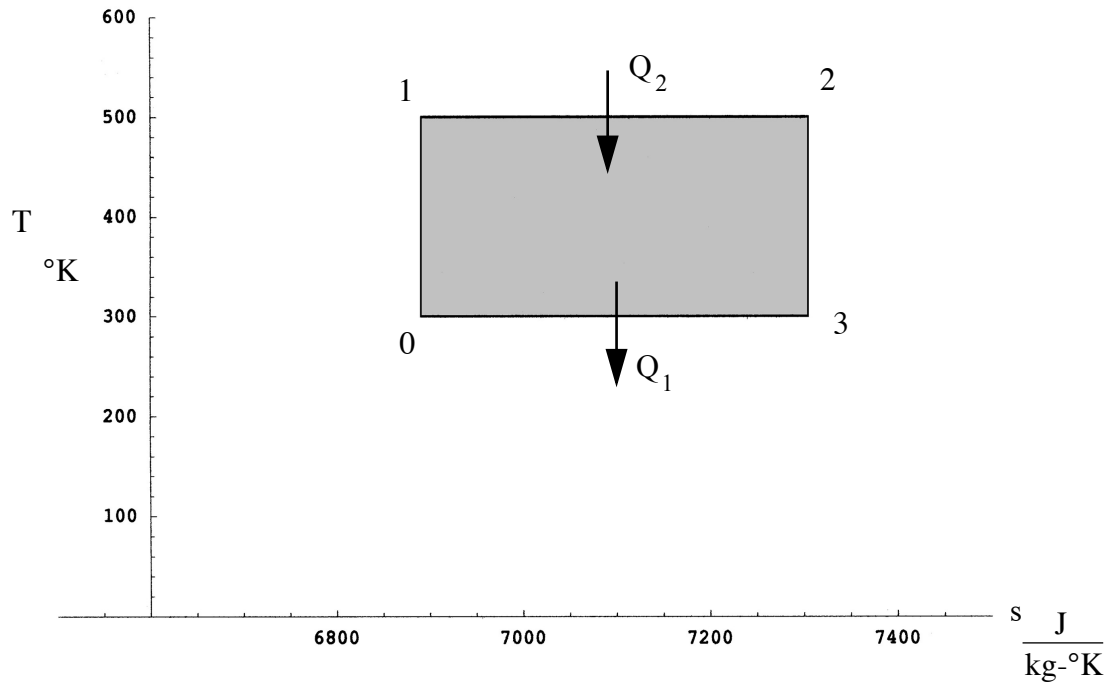*Figure 3.3   P-V diagram of the Carnot Cycle*

Figure 3.4   T-S diagram of the Carnot cycle

A concrete example in the P-V plane and T-S plane is shown in Figure 3.3 and Figure 3.4 above. The working fluid is nitrogen cycling between the temperatures of 300 and 500 Kelvin with the compression stroke moving between one and six atmospheres. The entropy per unit mass of the compression leg comes from tabulated data for nitrogen computed from Equation (3.120) below. The entropy per unit mass of the expansion leg is specified to be *7300 J/kg-°K* .

The thermodynamic efficiency of the cycle is

$$\eta \; = \; \frac{work \; output \; by \; the \; system \; during \; the \; cycle}{heat \; added \; to \; the \; system \; during \; the \; cycle} \; = \; \frac{W}{Q_2} \qquad (3.10)$$

According to the first law of thermodynamics

$$\delta Q \; = \; dE + \delta W . \qquad (3.11)$$

Over the cycle the change in internal energy (which is a state variable) is zero and the work done is

$$W \; = \; Q_2 + Q_1 \qquad (3.12)$$

where Q_1 is negative, and so the efficiency is

$$\eta = 1 + \frac{Q_1}{Q_2}. \tag{3.13}$$

The change in entropy per unit mass over the cycle is also zero and so from the Second Law

$$\oint ds = \oint \frac{\delta q}{T} = 0. \tag{3.14}$$

Since the temperature is constant during the heat interaction we can use this result to write

$$\frac{Q_1}{T_1} = -\frac{Q_2}{T_2} \tag{3.15}$$

Thus the efficiency of the Carnot cycle is

$$\eta_C = 1 - \frac{T_1}{T_2} < 1 \tag{3.16}$$

For the example shown $\eta_C = 0.4$. At most only 40% of the heat added to the system can be converted to work. The maximum work that can be generated by a heat engine working between two finite temperatures is limited by the temperature ratio of the system and is always less than the heat put into the system.

3.3.1   THE ABSOLUTE SCALE OF TEMPERATURE

For any Carnot cycle, regardless of the working fluid

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}. \tag{3.17}$$

Equation (3.17) enables an absolute scale of temperature to be defined that only depends on the general properties of a Carnot cycle and is independent of the properties of any particular substance.

As noted earlier the temperature, which is the integrating factor in the Gibbs equation (3.7), is only defined up to an arbitrary constant of proportionality. Similarly, any scale factor would divide out of (3.17) and so it has to be chosen by conven-

tion. The convention once used to define the Kelvin scale was to require that there be 100 degrees between the melting point of ice and the boiling point of water. Relatively recently there was an international agreement to define the ice point as exactly $273.15°K$ above absolute zero and allow the boiling point to be no longer fixed. As a result the boiling point of water is very nearly, but not exactly, $373.15°K$.

Absolute temperature is generally measured in degrees Rankine or degrees Kelvin and the scale factor between the two is

$$T_{Rankine} = \left(\frac{9}{5}\right) T_{Kelvin}. \tag{3.18}$$

The usual Farenheit and Centigrade scales are related to the absolute scales by

$$
\begin{aligned}
T_{Rankine} &= T_{Farenheit} + 459.67 \\
T_{Kelvin} &= T_{Centigrade} + 273.15
\end{aligned} \tag{3.19}
$$

3.4 ENTHALPY

It is often useful to rearrange Gibbs' equation so as to exchange dependent and independent variables. This can be accomplished using the so-called *Legendre transformation*. In this approach, a new variable of state is defined called the enthalpy per unit mass,

$$h = e + Pv \tag{3.20}$$

In terms of this new variable of state, the Gibbs equation becomes,

$$ds = \frac{dh}{T} - \frac{v}{T}dP \tag{3.21}$$

Using this simple change of variables, the pressure has been converted from a dependent variable to an independent variable.

$$ds(h, P) = \frac{dh}{T(h, P)} - \frac{v(h, P)}{T(h, P)}dP \tag{3.22}$$

Note that $1/T$ is still the integrating factor. With enthalpy and pressure as the independent variables the partial derivatives of the entropy are

$$\left.\frac{\partial s}{\partial h}\right|_{P\,=\,constant} = \frac{1}{T(h,\,P)} \qquad \left.\frac{\partial s}{\partial P}\right|_{h\,=\,constant} = -\frac{v(h,\,P)}{T(h,\,P)} \qquad (3.23)$$

and for any homogeneous material we can write

$$\frac{\partial^2 s}{\partial h\,\partial P} = \frac{\partial}{\partial P}\left(\frac{1}{T(h,\,P)}\right) = -\frac{\partial}{\partial h}\left(\frac{v(h,\,P)}{T(h,\,P)}\right) \qquad (3.24)$$

It is relatively easy to re-express Gibbs' equation with any two variables selected to be independent by defining additional variables of state, the free energy $f = e - Ts$ and the free enthalpy $g = h - Ts$ (also called the Gibbs free energy). The Gibbs free energy is very useful in the analysis of systems of reacting gases.

Using the Gibbs equation and an equation of state, any variable of state can be determined as a function of any two others. For example,

$$\begin{aligned}
e &= \phi(T,\,P) \;; & s &= \zeta(T,\,v) \\
g &= \xi(e,\,P) \;; & h &= \varphi(T,\,P) \\
s &= \theta(h,\,P) \;; & s &= \beta(e,\,v)
\end{aligned} \qquad (3.25)$$

and so forth.

3.4.1   GIBBS EQUATION ON A FLUID ELEMENT

One of the interesting and highly useful consequences of (3.25) is that any differentiation operator acting on the entropy takes on the form of Gibbs equation. Let

$$s = s(h(x,\,y,\,z,\,t),\,P(x,\,y,\,z,\,t)) \qquad (3.26)$$

Take the derivative of (3.26) with respect to time.

$$\frac{\partial s}{\partial t} = \frac{\partial s}{\partial h}\frac{\partial h}{\partial t} + \frac{\partial s}{\partial P}\frac{\partial P}{\partial t} \qquad (3.27)$$

Use (3.23) to replace $\partial s/\partial h$ and $\partial s/\partial P$, in equation (3.27).

$$\frac{\partial s}{\partial t} = \frac{1}{T(h,\,P)}\frac{\partial h}{\partial t} - \frac{v(h,\,P)}{T(h,\,P)}\frac{\partial P}{\partial t} \qquad (3.28)$$

This is essentially identical to Gibbs equation with the replacements

$$ds \rightarrow \partial s / \partial t$$
$$dh \rightarrow \partial h / \partial t \qquad (3.29)$$
$$dP \rightarrow \partial P / \partial t$$

Obviously, we could do this with any spatial derivative as well. For example

$$\frac{\partial s}{\partial x} = \frac{1}{T(h, P)} \frac{\partial h}{\partial x} - \frac{v(h, P)}{T(h, P)} \frac{\partial P}{\partial x}$$

$$\frac{\partial s}{\partial y} = \frac{1}{T(h, P)} \frac{\partial h}{\partial y} - \frac{v(h, P)}{T(h, P)} \frac{\partial P}{\partial y} \qquad (3.30)$$

$$\frac{\partial s}{\partial z} = \frac{1}{T(h, P)} \frac{\partial h}{\partial z} - \frac{v(h, P)}{T(h, P)} \frac{\partial P}{\partial z}$$

The three equations in (3.30) can be combined to form the gradient vector.

$$\boxed{\nabla s = \frac{\nabla h}{T} - \frac{v}{T} \nabla P} \qquad (3.31)$$

which is valid in steady or unsteady flow.

All these results come from the functional form (3.26) in which the entropy depends on space and time implicitly through the functions $h(x, y, z, t)$ and $P(x, y, z, t)$. The entropy does not depend explicitly on $x, y, z, \text{ or } t$.

Take the substantial derivative, D / Dt, of the entropy. The result is

$$\frac{\partial s}{\partial t} + \overline{U} \bullet \nabla s = \frac{1}{T} \left(\frac{\partial h}{\partial t} + \overline{U} \bullet \nabla h \right) - \frac{v}{T} \left(\frac{\partial P}{\partial t} + \overline{U} \bullet \nabla P \right) \qquad (3.32)$$

The result (3.32) shows how Gibbs equation enables a direct connection to be made between the thermodynamic state of a particular fluid element and the velocity field. One simply replaces the differentials in the Gibbs equation with the substantial derivative.

$$\boxed{\begin{array}{c} \dfrac{Ds}{Dt} = \dfrac{1}{T}\dfrac{Dh}{Dt} - \dfrac{v}{T}\dfrac{DP}{Dt} \\[4mm] \text{or} \\[4mm] \dfrac{Ds}{Dt} = \dfrac{1}{T}\dfrac{De}{Dt} - \dfrac{P}{\rho^2 T}\dfrac{D\rho}{Dt} \end{array}} \qquad (3.33)$$

Gibbs equation is the key to understanding the thermodynamic behavior of compressible fluid flow. Its usefulness arises from the fact that the equation is expressed in terms of perfect differentials and therefore correctly describes the evolution of thermodynamic variables over a selected fluid element without having to know the flow velocity explicitly. This point will be clarified as we work through the many applications to compressible flow described in the remainder of the text.

3.5 HEAT CAPACITIES

Consider the fixed volume shown below. An infinitesimal amount of heat per unit mass is added causing an infinitesimal rise in the temperature and internal energy of the material contained in the volume.
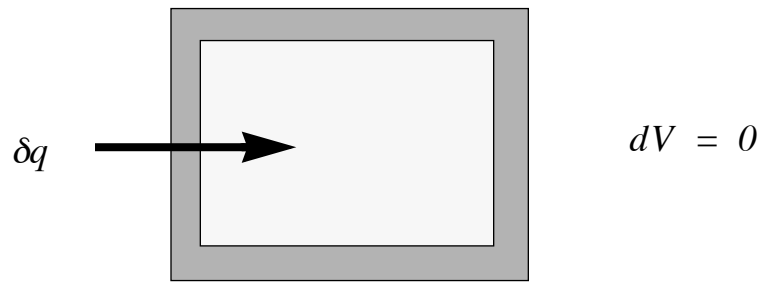
$$\delta q \qquad\qquad dV = 0$$

Figure 3.5   Heat addition at constant volume

The heat capacity at constant volume is defined as

$$C_v = \left.\frac{\delta q}{dT}\right|_{v = const} = \left.\frac{de + Pdv}{dT}\right|_{v = const} = \left.\frac{\partial e}{\partial T}\right|_{v = const} \qquad (3.34)$$

Now consider the piston cylinder combination shown below.
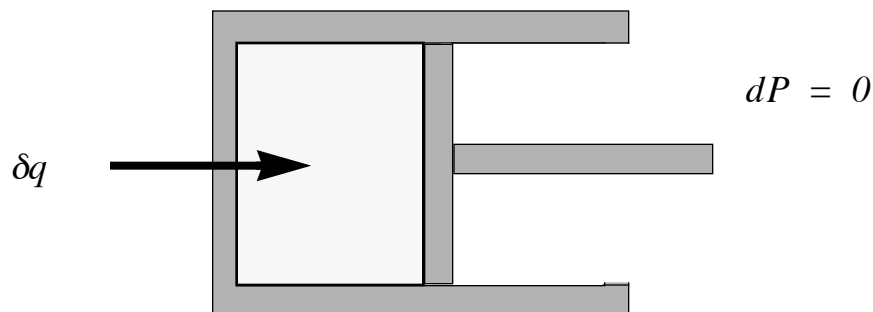
$$\delta q \qquad\qquad dP = 0$$

Figure 3.6   Heat addition at constant pressure

An infinitesimal amount of heat is added to the system causing an infinitesimal rise in temperature. There is an infinitesimal change in volume while the piston is withdrawn keeping the pressure constant. In this case the system does work on the outside world. The heat capacity at constant pressure is

$$C_p = \left.\frac{\delta q}{dT}\right|_{P\ =\ const} = \left.\frac{dh - vdP}{dT}\right|_{P\ =\ const} = \left.\frac{\partial h}{\partial T}\right|_{P\ =\ const} \tag{3.35}$$

For a process at constant pressure the heat added is used to increase the temperature of the gas *and* do work on the surroundings. As a result more heat is required for a given change in the gas temperature and thus $C_p > C_v$.

The enthalpy of a general substance can be expressed as

$$h(T, P) = \int^{T} C_p(T, P)dT + f(P) \tag{3.36}$$

where the pressure dependence needs to be determined by laboratory measurement. Heat capacities and enthalpies of various substances are generally tabulated purely as a functions of temperature by choosing a reference pressure of $P_{ref} = 10^5\ N/M^2$ for the integration. This leads to the concept of a standard enthalpy, $h°(T)$. The standard enthalpy can be expressed as

$$\tag{3.37}$$

$$h°(T) = \int_{0}^{T_{fusion}} C_p°dT + \Delta H_{fusion} + \int_{T_{fusion}}^{T_{vaporiz}} C_p°dT + \Delta H_{vaporiz} + \int_{vaporiz}^{T} C_p°dT$$

The heat capacity of almost all substances goes to zero rapidly as the temperature goes to zero and so the integration in (3.37) beginning at absolute zero generally does not present a problem. We shall return to the question of evaluating the enthalpy shortly after we have had a chance to introduce the concept of an ideal gas.

3.6 IDEAL GASES

For an ideal gas, the equation of state is very simple.

$$P = \frac{nR_uT}{V} \tag{3.38}$$

where n is the number of moles of gas in the system with volume, V. The universal gas constant is

$$R_u = 8314.472 \; Joules/(kmole - K) \tag{3.39}$$

It is actually more convenient for our purposes to use the gas law expressed in terms of the density.

$$\boxed{P = \rho RT} \tag{3.40}$$

where

$$R = R_u/M_w \tag{3.41}$$

and M_w is the mean molecular weight of the gas. The physical model of the gas that underlies (3.38) assumes that the gas molecules have a negligible volume and that the potential energy associated with intermolecular forces is also negligible. This is called the *dilute gas approximation* and is an excellent model over the range of gas conditions covered in this text.

For gas mixtures the mean molecular weight is determined from a mass weighted average of the various constituents. For air

$$\left.\begin{array}{l} M_w\big|_{air} = 28.9644 \; kilograms/kmole \\[2em] R = 287.06 \; m^2/sec^2 - K \end{array}\right\} \tag{3.42}$$

The perfect gas equation of state actually implies that the internal energy per unit mass of a perfect gas can only depend on temperature, $e = e(T)$. Similarly the enthalpy of a perfect gas only depends on temperature

$$h(T) = e + P/\rho = e(T) + RT \tag{3.43}$$

Since the internal energy and enthalpy only depend on temperature the heat capacities also depend only on temperature, and we can express changes in the internal energy and enthalpy as,

$$de = C_v(T)dT \quad ; \qquad dh = C_p(T)dT. \tag{3.44}$$

In this course we will deal entirely with ideal gases and so there is no need to distinguish between the standard enthalpy and enthalpy and so there is no need to use the distinguishing character "°".

Differentiate $RT = h(T) - e(T)$.

$$RdT = dh - de = (C_p - C_v)dT \tag{3.45}$$

The gas constant is equal to the difference between the heat capacities.

$$R = C_p - C_v \tag{3.46}$$

The heat capacities themselves are slowly increasing functions of temperature. But the gas constant is constant, as long as the molecular weight of the system doesn't change (there is no dissociation and no chemical reaction). Therefore the ratio of specific heats

$$\gamma = \frac{C_p}{C_v} \tag{3.47}$$

tends to decrease as the temperature of a gas increases.

All gases can be liquefied and the highest temperature at which this can be accomplished is called the critical temperature T_c. The pressure and density at the point of liquefaction are called the critical pressure P_c and critical density ρ_c. The critical temperature and pressure are physical properties that depend on the details of the intermolecular forces for a particular gas. An equation of state that takes the volume of the gas molecules and intermolecular forces into account must depend on two additional parameters besides the gas constant R. The simplest extension of the ideal gas law that achieves this is the famous van der Waals equation of state

$$P = \rho RT\left(\frac{1}{1 - b\rho} - \frac{a\rho}{RT}\right) \tag{3.48}$$

where

$$\frac{a}{b} = \frac{27}{8}RT_c \quad , \qquad \frac{a}{b^2} = 27P_c \tag{3.49}$$

The van der Waals equation provides a useful approximation for gases near the critical point where the dilute gas approximation loses validity.

3.7 CONSTANT SPECIFIC HEAT

The heat capacities of monatomic gases are constant over a wide range of temperatures. For diatomic gases the heat capacities vary only a few percent between the temperatures of 200°K and 1200°K. For enthalpy changes in this range one often uses the approximation of a *calorically perfect gas* for which the heat capacities are assumed to be constant and

$$e_2 - e_1 = C_v(T_2 - T_2) \quad ; \qquad h_2 - h_1 = C_p(T_2 - T_1) \tag{3.50}$$

For constant specific heat the Gibbs equation becomes

$$\frac{ds}{C_v} = \left(\frac{dT}{T}\right) - (\gamma - 1)\left(\frac{d\rho}{\rho}\right) \tag{3.51}$$

which can be easily integrated.

Figure 3.7 shows a small parcel of gas moving along some complicated path between two points in a flow. The thermodynamic state of the gas particle at the two endpoints is determined by the Gibbs equation.
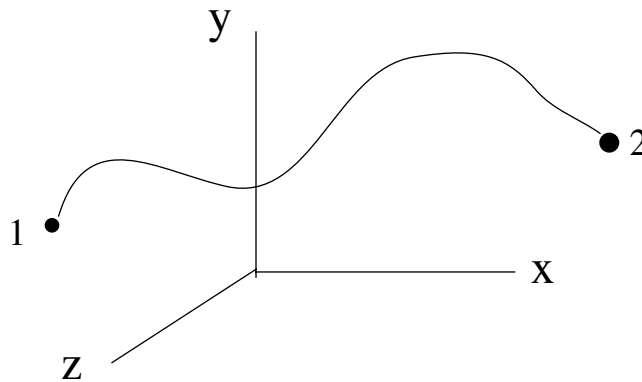

Figure 3.7   Conceptual path of a fluid element moving between two states.

Integrating (3.51) between 1 and 2 gives an expression for the entropy of an ideal gas with constant specific heats.

$$exp\left(\frac{s_2 - s_1}{C_v}\right) \ = \ \left(\frac{T_2}{T_1}\right)\left(\frac{\rho_2}{\rho_1}\right)^{-(\gamma - 1)}. \tag{3.52}$$

We can express Gibbs equation in terms of the enthalpy instead of internal energy.

$$ds \ = \ \frac{dh}{T} - \left(\frac{1}{\rho T}\right) dp \ = \ C_p \frac{dT}{T} - R\frac{dp}{p}. \tag{3.53}$$

Integrate between states 1 and 2.

$$exp\left(\frac{s_2 - s_1}{C_p}\right) \ = \ \left(\frac{T_2}{T_1}\right)\left(\frac{P_2}{P_1}\right)^{-\left(\frac{\gamma - 1}{\gamma}\right)}. \tag{3.54}$$

If we eliminate the temperature in (3.54) using the ideal gas law the result is

$$exp\left(\frac{s_2 - s_1}{C_v}\right) \ = \ \left(\frac{P_2}{P_1}\right)\left(\frac{\rho_2}{\rho_1}\right)^{-\gamma}. \tag{3.55}$$

In a process where the entropy is constant these relations become,

$$\frac{P_2}{P_1} \ = \ \left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{\gamma - 1}} \ ; \quad \frac{P_2}{P_1} \ = \ \left(\frac{\rho_2}{\rho_1}\right)^{\gamma} \ ; \quad \frac{\rho_2}{\rho_1} \ = \ \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma - 1}}. \tag{3.56}$$

Lines of constant entropy in P-T space are shown below.
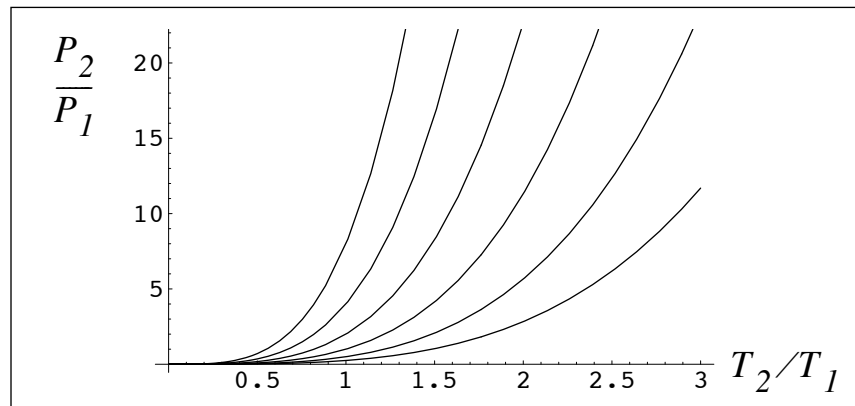

Figure 3.8   Lines of constant entropy for a calorically perfect gas.

The relations in (3.56) are sometimes called the *isentropic chain*.

Note that when we expressed the internal energy and enthalpy for a calorically perfect gas in (3.50) we were careful to express only changes over a certain temperature range. There is a temptation to simply express the energy and enthalpy as $e = C_v T$ and $h = C_p T$. This is incorrect! The correct values require the full integration from absolute zero shown in (3.37). As it happens, the gases we deal with in this course, air, oxygen, nitrogen, hydrogen, etc all condense at very low temperatures and so the contributions to the enthalpy from the condensed phase and phase change terms in (3.37) tend to be relatively small. This is also true for the monatomic gas helium in spite of the fact that, unlike virtually all other substances, its heat capacity becomes very large in a narrow range of temperatures near absolute zero.

3.8 THE ENTROPY OF MIXING

The second law of thermodynamics goes beyond the description of changes that relate solely to equilibrium states of a system and quantifies the distinction between reversible and irreversible processes that a system may undergo. For *any* change of a system

$$\delta q \le T ds \tag{3.57}$$

where ds is the change in entropy per unit mass. Substitute the first law in (3.57). For any change of a system

$$T ds \ge de + P dv . \tag{3.58}$$

Equation (3.58) is the basis of a complete theory for the equilibrium of a thermodynamic system. The incomplete notion of thermal equilibrium expressed by the zeroth law is only one facet of the vast range of phenomena covered by the second law (3.58).

3.8.1   SAMPLE PROBLEM - THERMAL MIXING

Equal *volumes* of an ideal gas are separated by an insulating partition inside an adiabatic container. The gases are at the same pressure but two different temperatures. Assume there are no body forces acting on the system (no gravitational effects).
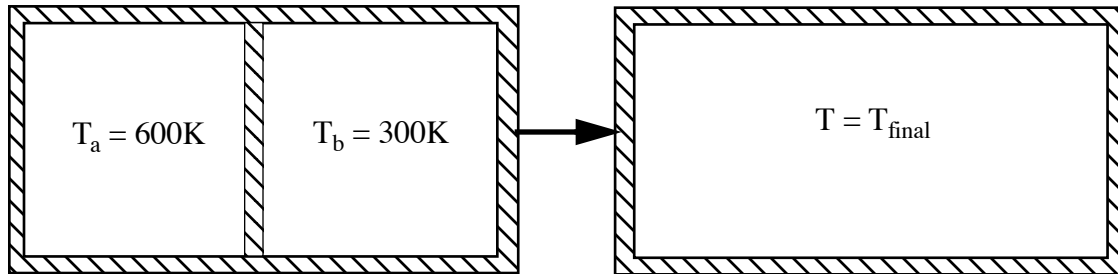

Figure 3.9   Thermal mixing of an ideal gas at two temperatures

The partition is removed and the temperature of the system is allowed to come to equilibrium.

1) What is the final temperature of the system?

Solution

Energy is conserved and all the gas energy is in the form of internal energy.

$$E - E_{ref} = m_a C_v (T_a - T_{ref}) + m_b C_v (T_b - T_{ref}) = (m_a + m_b) C_v (T_{final} - T_{ref}) \qquad (3.59)$$

Canceling the reference energies on both sides we can write

$$m_a C_v T_a + m_b C_v T_b = (m_a + m_b) C_v T_{final} \qquad (3.60)$$

The ideal gas law is

$$PV = m_a R T_a = m_b R T_b \qquad (3.61)$$

Rearrange (3.61) to read

$$\frac{m_b}{m_a} = \frac{T_a}{T_b} \qquad (3.62)$$

$$T_{final} = \frac{m_a T_a + m_b T_b}{(m_a + m_b)} = \frac{T_a + \left(\frac{m_b}{m_a}\right) T_b}{\left(1 + \frac{m_b}{m_a}\right)} = \frac{2T_a T_b}{T_a + T_b} = 400K \quad (3.63)$$

2) What is the change in entropy per unit mass of the system? Express your result in dimensionless form.

Solution

The process takes place at constant pressure. In this case the entropy change per unit mass of the two gases is

$$\frac{s_{final} - s_a}{C_p} = \ln\frac{T_{final}}{T_a}$$

$$\frac{s_{final} - s_b}{C_p} = \ln\frac{T_{final}}{T_b} \quad (3.64)$$

The entropy change per unit mass of the whole system is

$$\frac{s_{final} - s_{initial}}{C_p} = \frac{m_a\left(\frac{s_{final} - s_a}{C_p}\right) + m_b\left(\frac{s_{final} - s_b}{C_p}\right)}{m_a + m_b} \quad (3.65)$$

This can be expressed in terms of the initial and final temperatures as

$$\frac{s_{final} - s_{initial}}{C_p} = \frac{\ln\frac{T_f}{T_a} + \left(\frac{T_a}{T_b}\right)\ln\frac{T_f}{T_b}}{1 + \left(\frac{T_a}{T_b}\right)} = \frac{\ln\frac{400}{600} + (2)\ln\frac{400}{300}}{1 + (2)} \quad (3.66)$$

$$\frac{s_{final} - s_{initial}}{C_p} = \frac{-0.405465 + 2(0.28768)}{3} = 0.0566$$

The entropy of the system increases as the temperatures equalize.

3.8.2   ENTROPY CHANGE DUE TO MIXING OF DISTINCT GASES

The second law states that the entropy change of an *isolated* system undergoing a change in state must be greater than or equal to zero. Generally, non-equilibrium processes involve some form of mixing such as in the thermal mixing problem just discussed. Consider two ideal gases at equal temperatures and pressures separated by a partition that is then removed as shown below.
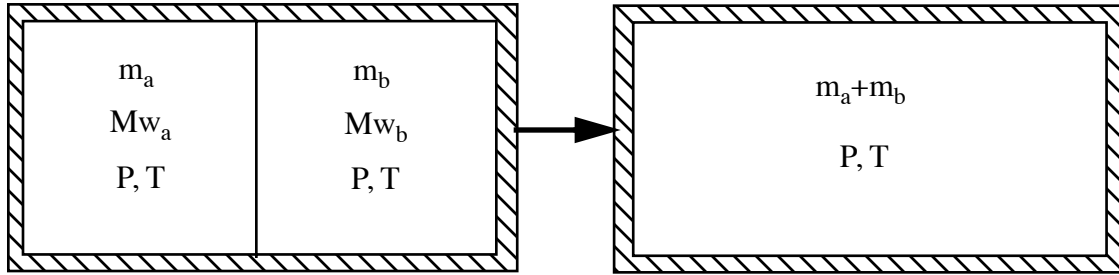

Figure 3.10   Mixing of two ideal gases at constant pressure and temperature.

For an ideal gas the Gibbs equation is

$$ds = C_p \frac{dT}{T} - R \frac{dP}{P} \tag{3.67}$$

The entropy per unit mass is determined by integrating the Gibbs equation.

$$s = \int C_p \frac{dT}{T} - R \ln P + \alpha \tag{3.68}$$

where α is a constant of integration. A fundamental question revolves around the evaluation of the entropy constant, α, for a given substance, . This is addressed by the third law of thermodynamics discussed in section 3.14.

For the two gases shown in the figure

$$s_a = \int C_{p_a} \frac{dT}{T} - \frac{R_u}{Mw_a} \ln P + \alpha_a$$

$$\tag{3.69}$$

$$s_b = \int C_{p_b} \frac{dT}{T} - \frac{R_u}{Mw_b} \ln P + \alpha_b$$

where $Mw_{a,b}$ refers to the molecular weights of the two distinctly different gases. The entropy of the whole system is

$$S = m_a s_a + m_b s_b \qquad (3.70)$$

Define the mass fractions

$$\chi_a = \frac{m_a}{m_a + m_b} \qquad \chi_b = \frac{m_b}{m_a + m_b} \qquad (3.71)$$

The overall entropy per unit mass before mixing is

$$s_{before} = \frac{S_{before}}{m_a + m_b} = \chi_a s_a + \chi_b s_b \qquad (3.72)$$

Substitute (3.69)

$$s_{before} = \chi_a \left(\int C_{P_a} \frac{dT}{T} - \frac{R_u}{Mw_a} \ln P + \alpha_a \right) + \chi_b \left(\int C_{P_b} \frac{dT}{T} - \frac{R_u}{Mw_b} \ln P + \alpha_b \right) \qquad (3.73)$$

After mixing each gas fills the whole volume V with the partial pressures given by

$$P_a = \frac{m_a}{V} \frac{R_u}{Mw_a} T \qquad P_b = \frac{m_b}{V} \frac{R_u}{Mw_b} T \qquad (3.74)$$

where

$$P = P_a + P_b \qquad (3.75)$$

The entropy of the mixed system is

$$s_{after} = \chi_a \left(\int C_{P_a} \frac{dT}{T} - \frac{R_u}{Mw_a} \ln P_a + \alpha_a \right) + \chi_b \left(\int C_{P_b} \frac{dT}{T} - \frac{R_u}{Mw_b} \ln P_b + \alpha_b \right) \qquad (3.76)$$

Therefore the entropy change of the system is

$$s_{after} - s_{before} = \chi_a \frac{R_u}{Mw_a} \ln \left(\frac{P}{P_a} \right) + \chi_b \frac{R_u}{Mw_b} \ln \left(\frac{P}{P_b} \right) > 0 \qquad (3.77)$$

The initially separated volumes were each in a state of local thermodynamic equilibrium. When the partition is removed the gases mix and until the mixing is complete the system is out of equilibrium. As expected the entropy increases. The nice feature of this example is that at every instant of the non-equilibrium process the pressure and temperature of the system are well defined.

By the way it should be noted that as long as the gases in Figure 3.10 are dilute and the enthalpy and internal energy depend only on temperature then the mixing process depicted in Figure 3.10 occurs adiabatically without any change in enthalpy or internal energy. If the gases are very dense so that intermolecular forces contribute to the internal energy then the enthalpy and internal energy depend on the pressure and the mixing process may release heat. In this case heat must be removed through the wall to keep the gas at constant temperature. This is called the heat of mixing. Throughout this course we will only deal with dilute gases for which the heat of mixing is negligible.

Gibbs paradox

If the gases in Figure 3.10 are identical, then there is no diffusion and no entropy change occurs when the partition is removed. But the full amount of entropy change is produced as long as the gases are different in any way no matter how slight. If we imagine a limiting process where the gas properties are made to approach each other continuously the same finite amount of entropy is produced at each stage until the limit of identical gases when it suddenly vanishes. This unexpected result is called Gibbs paradox after J.W. Gibbs who first noticed it.

However the atomistic nature of matter precludes the sort of continuous limiting process envisioned. As long as the two gases are different by any sort of experimental measurement whatsoever the full entropy change (3.77) is produced. This is true even if the two gases are chemically similar isotopes of the same element. For example, the inter-diffusion of ortho and para forms of hydrogen which differ only by the relative orientation of their nuclear and electronic spins would produce the same entropy increase. The entropy disappears only if the two molecules are identical.

A full understanding of this statement requires a combination of statistical thermodynamics and quantum mechanics. The founder of statistical mechanics is generally regarded to be Ludwig Boltzmann (1844-1906) an Austrian physicist who in 1877 established the relationship between entropy and the statistical model of molecular motion. Boltzmann is buried in the Central Cemetery in Vienna and on his grave marker is inscribed the equation

$$S = kLogW \tag{3.78}$$

that is his most famous discovery.

Boltzmann showed that the entropy is equal to a fundamental constant k times the logarithm of W which is equal to the number of possible states of the thermodynamic system with energy, E. A state of the system is a particular set of values for the coordinates and velocities of each and every molecule in the system.

Boltzmann's constant is essentially the universal gas constant per molecule.

$$k = R_u/N \tag{3.79}$$

where N is Avagadro's number. For a monatomic ideal gas, statistical mechanics gives

$$W \approx V^{N_p} E^{\frac{3N_p}{2}} \tag{3.80}$$

where V is the volume and N_p is the number of atoms in the system. When (3.80) is substituted into (3.78) the result is

$$S \approx R_u Log(V(C_v T)^{3/2}) \tag{3.81}$$

which is essentially the same expression that would be generated from Gibbs equation. See Appendix 1 for more detail.

When a volume of gas molecules is analyzed using quantum mechanics the energy of the system is recognized to be quantized and the statistical count of the number of possible states of the system is quite different depending on whether the individual molecules are the same or not. If the molecules are different the number of possible states for a given energy is much larger and this is the basis for the explanation of the Gibbs paradox.

3.9 ISENTROPIC EXPANSION

3.9.1   BLOWDOWN OF A PRESSURE VESSEL

Consider the blowdown through a small hole of a calorically perfect gas from a large adiabatic pressure vessel at initial pressure P_i and temperature T_i to the surroundings at pressure P_a and temperature T_a.
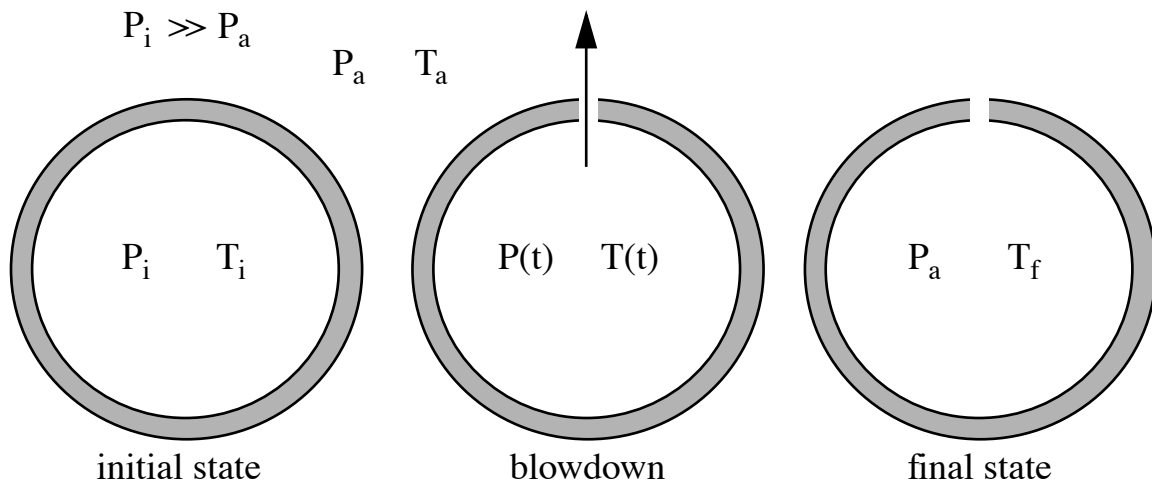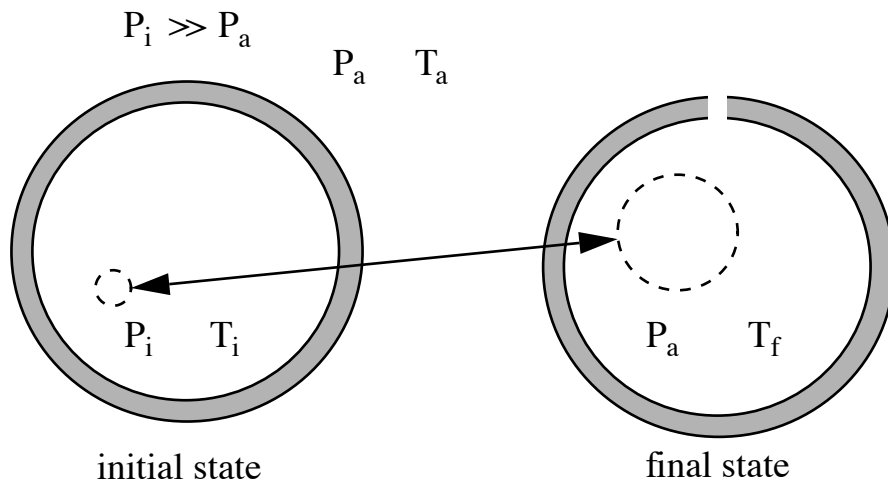

Figure 3.11   A spherical, thermally insulated pressure vessel exhausts to the surroundings through a small hole.

(1) Determine the final temperature of the gas in the sphere.

Solution

Imagine a parcel of gas that remains inside the sphere during the expansion process as shown below.

initial state   final state

As long as the gas is not near the wall where viscosity might play a role, the expansion of the gas parcel is nearly isentropic. The final temperature is

$$\frac{T_f}{T_i} = \left(\frac{P_a}{P_i}\right)^{\frac{\gamma - 1}{\gamma}}$$

(3.82)

(2) Determine the entropy change per unit mass during the process for the gas ejected.

Solution

The ejected gas mixes with the infinite surroundings and comes to a final temperature and pressure, T_a and P_a. The entropy change is

$$\frac{s_f - s_i}{C_p} = Log\left(\frac{T_a}{T_i}\right) - \left(\frac{\gamma - 1}{\gamma}\right)Log\left(\frac{P_a}{P_i}\right)$$

(3.83)

3.9.2 WORK DONE BY AN EXPANDING GAS

The gun tunnel is a system for studying the flow over a projectile at high speed in rarefied conditions typical of very high altitude flight. High pressure gas is used to accelerate the projectile down a gun barrel. The projectile exits into a large chamber at near vacuum pressure. The figure below depicts the situation.
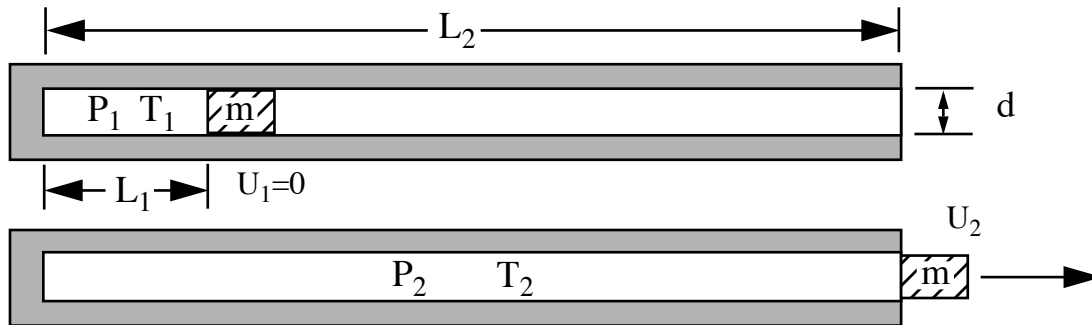

Figure 3.12   Projectile energized by an expanding gas

We wish to determine the kinetic energy of the projectile when it exits into the vacuum chamber. The work done by the gas on the projectile is equal to the kinetic energy of the projectile.

$$W = \int_{L_1}^{L_2} P dV = \frac{1}{2} m U_2^2 \tag{3.84}$$

where the friction between the projectile and the gun barrel has been neglected as well as any work done against the small pressure in the vacuum chamber.

In order to solve this problem it is necessary to postulate a relationship between the gas pressure in the gun barrel and the volume. The simplest approach is to assume that the gas expands isentropically. In this case the pressure and density of the gas behind the projectile are related by

$$\frac{P}{P_1} = \left(\frac{\rho}{\rho_1}\right)^\gamma = \left(\frac{\dfrac{4m_{gas}}{\pi d^2 L}}{\dfrac{4m_{gas}}{\pi d^2 L_1}}\right)^\gamma = \left(\frac{L_1}{L}\right)^\gamma \tag{3.85}$$

where m_{gas} is the mass of the gas expanding behind the projectile. The work integral (3.84) becomes

$$\frac{1}{2}mU_2^2 = \left(\frac{\pi d^2}{4}\right)\int_{L_1}^{L_2} P_1\left(\frac{L_1}{L}\right)^\gamma dL. \tag{3.86}$$

Carry out the integration

$$\frac{1}{2}mU_2^2 = \left(\frac{\pi d^2}{4}\right)\frac{P_1 L_1^\gamma}{1-\gamma}(L_2^{1-\gamma} - L_1^{1-\gamma}) \tag{3.87}$$

or

$$\frac{1}{2}mU_2^2 = \left(\frac{\pi d^2 L_1}{4}\right)\frac{P_1}{\gamma-1}\left(1 - \left(\frac{L_1}{L_2}\right)^{\gamma-1}\right) \tag{3.88}$$

The first term in brackets on the right side of (3.88) is the initial volume of gas

$$V_1 = \frac{\pi d^2 L_1}{4}. \tag{3.89}$$

Using (3.89) equation (3.88) takes the form

$$\frac{1}{2}mU_2^2 = \frac{P_1 V_1}{\gamma-1}\left(1 - \left(\frac{L_1}{L_2}\right)^{\gamma-1}\right) \tag{3.90}$$

Replace $P_1 V_1$ with $m_{gas}RT_1$ and recall that $R = C_p - C_v$ and $\gamma = C_p/C_v$. The kinetic energy of the projectile when it leaves the barrel is

$$\frac{1}{2}mU_2^2 = m_{gas}C_v T_1\left(1 - \left(\frac{L_1}{L_2}\right)^{\gamma-1}\right) \tag{3.91}$$

Note that in the limit where the barrel of the gun is extremely long so that $L_1/L_2 \ll 1$ all of the gas thermal energy is converted to kinetic energy of the projectile.

3.9.3   EXAMPLE - HELIUM GAS GUN

Suppose the tunnel is designed to use Helium as the working gas. The gas is introduced into the gun barrel and an electric arc discharge is used to heat the Helium to very high pressure and temperature. Let the initial gas pressure and temperature be $P_1 = 4 \times 10^8 N/M^2$ and $T_1 = 2000°K$. The initial length is $L_1 = 0.1\,M$, the final length is $L_2 = 2\,M$ and the barrel diameter is $d = 0.04\,M$. The projectile mass is $0.1\,kg$. Determine the exit velocity of the projectile. Compare the exit velocity with the speed of sound in the gas at the beginning and end of the expansion.

Solution

Helium is a monatomic gas with an atomic mass of 4.0026. The mass of Helium used to drive the projectile is determined from the ideal gas law

$$P_1 V_1 = m_{gas} \left(\frac{R_u}{M_w} \right) T_1 . \qquad (3.92)$$

or

$$m_{gas} = \frac{P_1 V_1}{T_1} \left(\frac{M_w}{R_u} \right) = \frac{4 \times 10^8}{2000} \left(\frac{\pi (0.04)^2 (0.1)}{4} \right) \left(\frac{4.0026}{8314.472} \right) = 0.01208\,Kg \qquad (3.93)$$

The velocity of the projectile at the exit of the barrel is

$$U_2 = \left[2 \left(\frac{0.01208}{0.1} \right) \left(\frac{3}{2} \right) \left(\frac{8314.472}{4.0026} \right) (2000) \left(1 - \left(\frac{0.1}{2} \right)^{\frac{2}{3}} \right) \right]^{\frac{1}{2}} = 1140.7\,M/Sec . \qquad (3.94)$$

where the relation $C_v = (3/2)R$ has been used. Note that the final projectile speed is fairly small compared to the initial speed of sound in the gas,

$$a_1 = \sqrt{\gamma R T_1} = 2631\,M/Sec . \qquad (3.95)$$

The temperature of the gas at the end of the expansion is determined using the isentropic relations (3.56).

$$T_2 = T_1 \left(\frac{L_1}{L_2}\right)^{\gamma-1} = 2000\left(\frac{0.1}{2}\right)^{2/3} = 271 \ K. \tag{3.96}$$

The corresponding speed of sound is

$$a_1 = \sqrt{\gamma R T_2} = 968 \ M/Sec. \tag{3.97}$$

The main assumption used to solve this problem is embodied in the use of (3.85) to determine the pressure behind the projectile. This equation effectively neglects the motion of the gas and assumes that the pressure, temperature and density are uniform over the volume behind the projectile during the expansion. This is an excellent assumption if the expansion is slow but not so good if the expansion is fast. But fast compared to what? This is where the speed of sound calculation comes in. If the projectile speed is small compared to the sound speed, a, then the gas speed over the length of the barrel must also be small compared to a. In that limit the pressure variation is also small and the uniform property assumption works quite well. But notice that by the end of the expansion the speed of the projectile exceeds the speed of sound. A more accurate treatment of this problem requires a full analysis of the unsteady gasdynamics of the flow.

3.9.4   ENTROPY INCREASE DUE TO VISCOUS FRICTION

In the gas gun example viscous friction is an important generator of entropy. The gas behind the projectile, away from the barrel wall is moving at very high speed but the gas near the wall is subject to the no slip condition. In the small gap between the projectile and the barrel the flow is similar to the Couette flow considered in the last chapter. Everywhere near the wall the flow is subject to very high shear rates leading to high viscous stresses.

So far we have seen how gradients in temperature and gas concentration lead to an increase in the entropy. In Chapter 7 we will show that flow kinetic energy dissipation due to viscous friction *always* leads to an increase in the entropy per unit mass. An accurate calculation of viscous effects in the gun tunnel problem requires a numerical analysis of the full viscous equations of motion and remains today a difficult research problem.

One of the most difficult challenges in the development of new power and propulsion systems is the accurate prediction of entropy changes in the system. Literally billions of dollars are spent by manufacturers in the pursuit of small reductions in the entropy generated in compressors and turbines and small excesses can spell the difference between success and failure of a new design.

3.10 SOME RESULTS FROM STATISTICAL MECHANICS

A discussion of this topic can be found in the Appendix. Here we shall state the main results that will be used in our investigations of compressible flow.

Classical statistical mechanics leads to a simple expression for C_p and C_v in terms of β, the number of degrees of freedom of the appropriate molecular model.

$$C_p = \frac{\beta + 2}{2}R \ ; \qquad C_v = \frac{\beta}{2}R \ ; \qquad \gamma = \frac{\beta + 2}{\beta} \qquad (3.98)$$

For a mass point, m, with three translational degrees of freedom and no internal structure, $\beta = 3$. The law of equipartition of energy says that any term in the expression for the energy of the mass point that is quadratic in either the position or velocity contributes $(1/2)kT$ to the thermal energy of a large collection of such mass points. Thus the thermal energy (internal energy) per molecule of a gas composed of a large collection of mass points is

$$\tilde{e} = (3/2)kT \qquad (3.99)$$

where k is Boltzmann's constant,

$$k = 1.3806505 \times 10^{-23} Joules/K. \qquad (3.100)$$

Over one mole of gas,

$$N\tilde{e} = (3/2)R_u T \qquad (3.101)$$

where $R_u = Nk$ is the universal gas constant and N is Avogadro's number,

$$N = 6.0221415 \times 10^{26} \ molecules/kmole. \qquad (3.102)$$

On a per unit mass of gas basis the internal energy is,

$$e = (3/2)RT \qquad (3.103)$$

This is a good model of monatomic gases such as Helium, Neon, Argon, etc. Over a very wide range of temperatures,

$$C_p = \frac{5}{2}R \quad ; \qquad C_v = \frac{3}{2}R \tag{3.104}$$

from near condensation to ionization.

3.10.1 DIATOMIC GASES

At room temperature, diatomic molecules exhibit two additional rotational degrees of freedom and

$$C_p = \frac{7}{2}R \quad ; \qquad C_v = \frac{5}{2}R \tag{3.105}$$

At very low temperatures, C_p can decrease below $(7/2)R$ because rotational degrees of freedom can freeze out - a phenomenon that can only be understood using quantum statistical mechanics. However, for N_2 and O_2 the theoretical transition temperature is in the neighborhood of 3 degrees Kelvin, well below the temperature at which both gases liquefy. For H_2 the transition temperature is about 90K.

At high temperatures, C_p can increase above $(7/2)R$ because the atoms are not rigidly bound but can vibrate. This brings into play two additional vibrational degrees of freedom. At high temperatures the heat capacities approach

$$C_p = \frac{9}{2}R \quad ; \qquad C_v = \frac{7}{2}R \tag{3.106}$$

3.10.2 CHARACTERISTIC VIBRATIONAL TEMPERATURE

The determination of the temperature at which the specific heat changes from $(7/2)R$ to $(9/2)R$ is also beyond classical statistical mechanics but can be determined using quantum statistical mechanics. The specific heat of a diatomic gas from room temperature up to high combustion temperatures is accurately predicted from theory to be

$$\frac{C_p}{R} = \frac{7}{2} + \left\{ \frac{(\theta_v/2T)}{Sinh(\theta_v/2T)} \right\}^2 . \tag{3.107}$$

The characteristic vibrational temperatures for common diatomic gases are

$$\theta_v\big|_{O_2} = 2238K \quad ; \quad \theta_v\big|_{N_2} = 3354K \quad ; \quad \theta_v\big|_{H_2} = 6297K. \tag{3.108}$$

The increasing values of θ_v with decreasing molecular weight reflect the increasing bond strength as the interatomic distance decreases.

3.11 ENTHALPY - DIATOMIC GASES

The enthalpy of a diatomic gas is

$$h(T) - h(T_{ref}) = \int_{T_{ref}}^{T} C_p dT = R\int_{T_{ref}}^{T} \left[\frac{7}{2} + \left\{\frac{(\theta_v/2T)}{Sinh(\theta_v/2T)}\right\}^2\right] dT \tag{3.109}$$

This integrates to

$$\frac{h(T)}{R\theta_v} - \frac{h(T_{ref})}{R\theta_v} = \frac{7}{2}\left(\frac{T - T_{ref}}{\theta_v}\right) + \frac{1}{\left(e^{(\theta_v/T)} - 1\right)} - \frac{1}{\left(e^{(\theta_v/T_{ref})} - 1\right)} \tag{3.110}$$
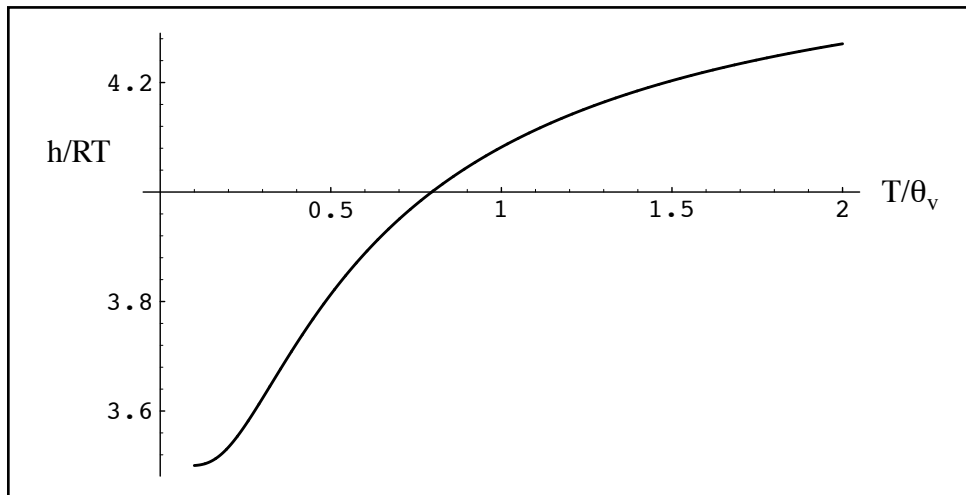
The enthalpy is plotted below for $T_{ref} = 0$.

Figure 3.13   Enthalpy versus temperature for a diatomic gas

3.12 SPEED OF SOUND

The speed of sound in a homogeneous medium is,

$$a^2 = \left. \left(\frac{\partial P}{\partial \rho} \right) \right|_{s \,=\, constant} \tag{3.111}$$

For an ideal gas,

$$a^2 = \frac{\gamma P}{\rho} = \gamma R T \tag{3.112}$$

For a flow at velocity U the Mach number is

$$M = \frac{U}{\sqrt{\gamma R T}} \tag{3.113}$$

3.13 ATMOSPHERIC MODELS

In a stable atmosphere where the fluid velocity is zero, the pressure force on a fluid element is balanced by the force of gravity.

$$\nabla P = -\rho \nabla \Psi \tag{3.114}$$

where Ψ is the gravitational potential. Near the Earth's surface the variation of gravitational acceleration with height is relatively small and so we can write

$$\frac{dP}{dz} = -\rho g \tag{3.115}$$

where $g = 9.80665 M / sec^2$ and z is the height above the ground.

In an atmosphere where the entropy is constant the pressure and density at a given height are related by

$$\frac{P}{P_0} = \left(\frac{\rho}{\rho_0} \right)^\gamma \tag{3.116}$$

where P_0 and ρ_0 are the pressure and density at ground level. Use (3.116) to replace the pressure in (3.115). The resulting equation can be integrated from the ground to a height z and the result is

$$\frac{\rho}{\rho_0} = \left(1 - (\gamma - 1)\frac{gz}{a_0^2}\right)^{\frac{1}{\gamma - 1}} \tag{3.117}$$

In this model the atmospheric density decreases algebraically with height and goes to zero (vacuum) when $gz/a_0^2 = 1/(\gamma - 1)$.

An alternative model that is more accurate in the upper atmosphere is to assume that the atmosphere is isothermal. In this case the pressure and density are related by the ideal gas law $P = \rho RT$ where the temperature is constant at the ground value $T = T_0$. In this case (3.115) integrates to

$$\frac{\rho}{\rho_0} = e^{-\frac{\gamma gz}{a_0^2}} \tag{3.118}$$

The length scale

$$H = \frac{a_0^2}{\gamma g} = \frac{RT_0}{g} \tag{3.119}$$

is called the scale height of the atmosphere. Roughly speaking it is the height where the gravitational potential energy of a fluid element is comparable to its thermal energy. For Air at $288.15K$ the scale height is $8435m$.
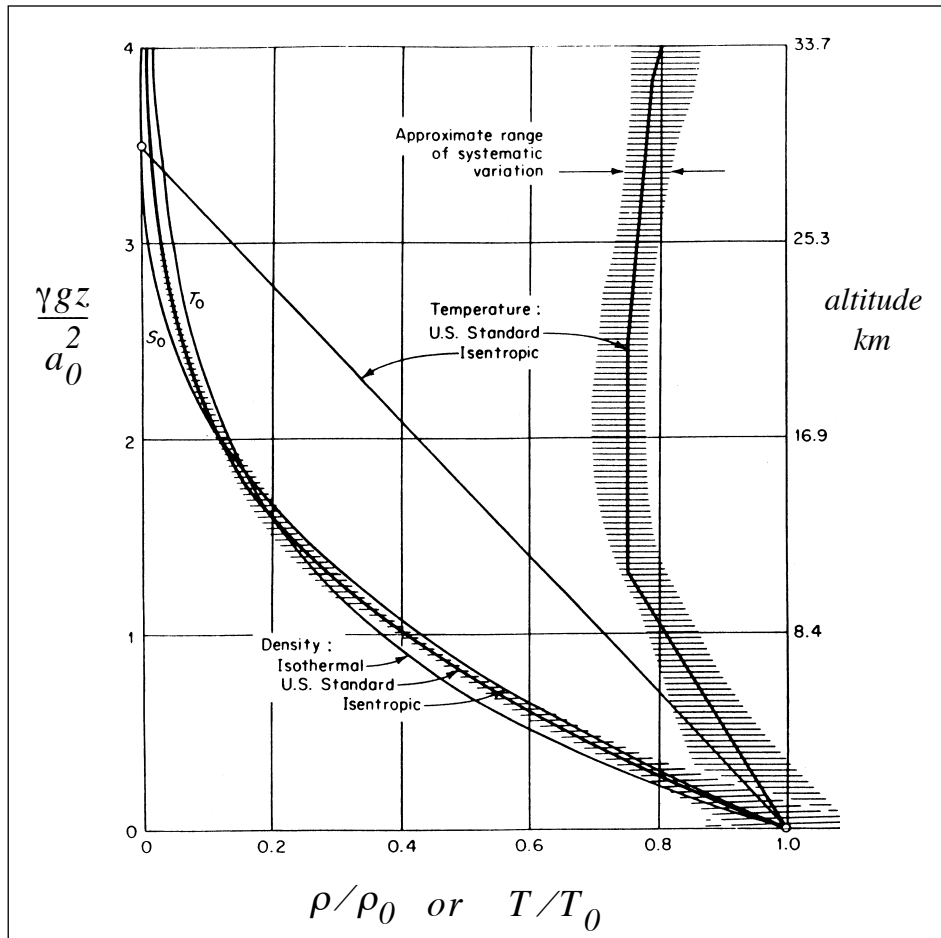
Figure 3.14   Density and temperature of the standard atmosphere.

How accurate are these models? A comparison is shown in Figure 3.14. Note that the two models tend to bracket the actual behavior of the atmosphere. Below a scale height of one, the atmosphere is approximately isentropic and the temperature falls off almost linearly. Above a scale height of about 1.5 the temperature is almost constant.

3.14 THE THIRD LAW OF THERMODYNAMICS

The first law is a statement of conservation of energy and shows that heat and work can be exchanged with one another. The second law restricts the possible occurrence of certain processes and can be utilized to predict the direction of a process. Moreover, the second law shows that no engine can be built that converts all the

input heat energy to an equal amount of useful work. The first and second laws are well supported by a long history of agreement with experimental measurements in a vast variety of applications.

The third law of thermodynamics is still a source of leading edge research in the thermodynamics of materials. It was first formulated by the German physicist Walther Hermann Nernst in 1906 whose work won him the Nobel prize for Chemistry in 1920. One statement of the Nernst theorem is that the entropy of a system at zero absolute temperature is a well-defined constant. Another statement is that the entropy of a pure perfect crystalline solid at absolute zero is zero.

The standard entropy of a gas at the standard pressure ($10^5 N/m^2$) is determined by integrating the Gibbs equation,

$$(3.120)$$

$$S°(T) \ = \ \int_0^{T_{fusion}} C_p° \frac{dT}{T} + \frac{\Delta H_{fusion}}{T_{fusion}} + \int_{T_{fusion}}^{T_{vaporiz}} C_p° \frac{dT}{T} + \frac{\Delta H_{vaporiz}}{T_{vaporiz}} + \int_{vaporiz}^{T} C_p° \frac{dT}{T}$$

The heats of fusion and vaporization in (3.120) are at standard pressure. The third law of thermodynamics requires that the heat capacity $C_p \rightarrow 0$ as $T \rightarrow 0$ at a rate that is fast enough to insure convergence of the first integral in (3.120). Calorimetric measurements show that $C_p \approx T^3$ for nonmetals at very low temperatures.

For metals C_p is proportional to T^3 at low temperatures but becomes proportional to T at extremely low temperatures. At very low temperature the atomic motion in a metallic crystal freezes out and the residual heat capacity comes from the motion of the conduction electrons in the metal.

Experimentally it does appear that the entropy at absolute zero approaches the same constant value for all pure substances. The third law codifies this result and sets $S(0) = 0$ for all pure elements and compounds in their most stable, perfect crystalline state at absolute zero. So for example the entropy of water vapor at *125C* and one atmosphere would be calculated from heat capacity data as follows.

$$S°(398.15) = 0 + \int_0^{273.15} C_p°\frac{dT}{T} + \frac{\Delta H_{fusion}}{273.15} + \int_{273.15}^{373.15} C_p°\frac{dT}{T} +$$

$$\frac{\Delta H_{vaporiz}}{373.15} + \int_{373.15}^{398.15} C_p°\frac{dT}{T}$$

(3.121)

This calculation assumes that the ice crystal is perfect. From a quantum mechanical viewpoint a perfect crystal at zero temperature would exist in only one (nonzero) energy state. The Boltzmann relation (3.78) would reduce to $S(0) = kLog(1) = 0$ which is consistent with the Nernst theorem.

In a pure, perfect crystal there is no entropy of mixing but in a mixed crystal containing atomic or molecular species A and B there are different ways A and B can be arranged and so the entropy at absolute zero is not zero.

The entropy at absolute zero is called the residual entropy. There can be a significant residual entropy in a variety of common substances where imperfections can occur due to variations in the molecular orientation. Glasses (that are amorphous materials) and alloys (that are mixtures of metals) also have residual entropy. The determination of the residual entropy can be quite complex and is responsible for deviations between calculated and experimental values of the entropy.

Even in the case of a pure solid if the crystal is not perfect the entropy is nonzero. For example, the CO molecule has a small dipole moment and so there is a finite probability that, as it freezes, the molecules can align in the crystal as CO-OC-CO instead of CO-CO-CO. A given crystal will contain a mixture of both types of alignment and so it is not perfect and the entropy at $0°K$ is not zero.

All these matters are the subject of ongoing research. In virtually all applications of thermodynamics to compressible flow the interesting result is based on *changes* in entropy associated with some process such as the mixing problem described in Section 3.8. Such changes are unaffected by possible errors in the entropy constant.

3.15 PROBLEMS

Problem 1 - Use the Gibbs equation to determine each of the following for an ideal gas.

$$\left(\frac{\partial s(T, \rho)}{\partial T}\right)_{\rho} = \qquad \left(\frac{\partial s(T, \rho)}{\partial \rho}\right)_{T} =$$

$$\left(\frac{\partial s(T, P)}{\partial T}\right)_{P} = \qquad \left(\frac{\partial s(T, P)}{\partial P}\right)_{T} = \qquad (3.122)$$

Problem 2 - In Section 2 it was stated that the internal energy and enthalpy of an ideal gas depend only on temperature. Show that this is true. First show that for an ideal gas the Gibbs equation can be written in the form

$$ds(T, P) = \frac{1}{T}de(T, P) + \frac{R}{T}dT - \frac{v}{T}dP \qquad (3.123)$$

Work out the partial derivatives of the entropy, and show by the cross-derivative test that $\partial e(T, P)/\partial P = 0$.

Problem 3 - Use the Gibbs equation to show that for a general substance.

$$\left(\frac{\partial h}{\partial P}\right)_{T} = -T\frac{\partial v(T, P)}{\partial T} + v(T, P) \qquad (3.124)$$

where $v(T, P)$ is the volume per unit mass.

Problem 4 - The temperature, entropy and pressure in a calorically perfect ideal gas moving in an unsteady, three-dimensional flow are related by the function

$$exp\left(\frac{s - s_{ref}}{C_p}\right) = \left(\frac{T}{T_{ref}}\right)\left(\frac{P}{P_{ref}}\right)^{-\left(\frac{\gamma - 1}{\gamma}\right)}. \qquad (3.125)$$

Take the gradient of (3.125) and show directly that the flow satisfies.

$$T\nabla s = \nabla h - \frac{\nabla P}{\rho} \qquad (3.126)$$

Problem 5 - Show that the internal energy of a van der Waals gas is of the form $e(T, v) = f(T) - a/v$.

Problem 6 - A heavy piston is dropped from the top of a long, insulated, vertical shaft containing air. The shaft above the piston is open to the atmosphere. Determine the equilibrium height of the piston when it comes to rest. Feel free to introduce whatever data or assumptions you feel are required to solve the problem. Suppose you actually carried out this experiment. How do you think the measured height of the piston would compare with your model?

Problem 7 - In problem 6 what would be the equilibrium height if the gas in the shaft is Helium.

Problem 8 - Consider the nearly isentropic flow of an ideal gas across a low pressure fan such as an aircraft propeller. Assume that the pressure change ΔP is small. Show that the corresponding density change is

$$\frac{\Delta \rho}{\rho_0} \approx \frac{1}{\gamma} \frac{\Delta P}{P_0} \tag{3.127}$$

where ρ_0 and P_0 are the undisturbed values ahead of the fan.

Problem 9 - Mars has an atmosphere that is about 96% Carbon Dioxide at a temperature of about 200K. Determine the scale height of the atmosphere and compare it with Earth. The pressure at the surface of Mars is only about 1000 Pascals. Entry, descent and landing of spacecraft on Mars is considered to be in some ways more difficult than on Earth. Why do you think this is?

Problem 10 - Suppose you are driving and a child in the back seat is holding a Helium filled balloon. You brake for a stoplight. In surprise the child releases the balloon. The x-momentum equation governing the motion of the air in the car can be simplified to

$$\rho \frac{\partial U}{\partial t} = -\frac{\partial P}{\partial x}. \tag{3.128}$$

Use this result to show in which direction the balloon moves. What assumptions are needed to reduce the momentum equation to (3.128)? Compare this problem to the material developed in Section 2.13