Chapter 2

A Minimum of Thermodynamics
and of
Kinetic Theory of Gases

2.1 The Motion of Molecules

A gas is a collection of particles (molecules) that to a first approximation interact with one another solely through elastic collisions—in other words, through collisions that conserve both energy and momentum. If molecules were dimensionless, point-like objects, their thermal energy would be only that of linear motion in three dimensions—they would have only *three degrees of freedom.* In reality, molecules are more complicated. Even a simple monatomic one, such as helium, may be able to spin (because it has a finite dimension) and may, therefore, have more than three degrees of freedom. Multiatomic molecules can also vibrate and this confers to them additional degrees of freedom.

At a given moment, some molecules have large kinetic energy, while others have little. However, over a sufficiently long period of time, each has the same *average kinetic energy*, $<W_{mol}>$. This intuitive result is called the **principle of equipartition of energy**. What is not so immediately obvious is that the principle applies even to a collection of molecules with different masses: the more massive ones will have smaller average velocities than the lighter ones, but their average energy will be the same. According to this principle, the energy associated with any degree of freedom is the same. The instantaneous velocities have a **Maxwellian** distribution, as discussed in Section 2.28.

2.2 Temperature

It is useful to distinguish the two components of the average molecular energy: $< W_{mol,\ linear} >$ and $< W_{mol,\ spin\ \&\ vibr.} >$,

$$< W_{mol} >=< W_{mol,\ linear} > + < W_{mol,\ spin\ \&\ vibr.} > \tag{1}$$

The pressure a gas exerts on an obstacle is the result of molecules colliding with the obstacle. Clearly, only the *linear* motion of the molecules can contribute to pressure; spin and vibration do not.

Temperature is a measure of $<W_{mol,\ linear}>$. It is defined by

$$T = \frac{2}{3k} < W_{mol,\ linear} > . \tag{2}$$

The factor $\frac{1}{3}$ in the proportionality constant, $\frac{2}{3k}$, results from the three degrees of freedom. k is **Boltzmann's constant** and has, of course, the dimensions of energy per temperature (in the SI, $k = 1.38 \times 10^{-23}$ joules/kelvin).

In terms of temperature, the average energy of linear molecular motion in a three-dimensional gas is

$$<W_{mol,\ linear}>= 3\frac{k}{2}T \tag{3}$$

and, per degree of freedom,

$$<W_{mol,\ linear,\ per\ deg.\ of\ freed.}>= \frac{k}{2}T \tag{4}$$

Since each degree of freedom (associated with linear motion, spin, or with vibration), has the same energy, the average total molecular energy is

$$<W_{mol}>= \frac{\nu}{2}kT, \tag{5}$$

where ν is the number of degrees of freedom.

2.3 The Perfect-Gas Law

It is obvious that a simple relationship must exist between pressure and temperature. Consider motion in a single dimension normal to a surface. Upon impact, the molecule deposits a momentum of $2mv$ on the wall (the factor 2 accounts for the impinging velocity being v and the reflected velocity being another v). The flux of molecules (i.e., the number of molecules moving through a unit area in unit time) is $\frac{1}{2}nv$, where n is the **concentration** of molecules (i.e., the number of molecules per unit volume). Here the $\frac{1}{2}$ accounts for half the molecules moving in one direction, while the other half moves in the opposite direction because we are assuming that there is no net flux—that is, no bulk gas motion. The rate of change of momentum per unit area per unit time, i.e., the pressure exerted by the gas is, thus,

$$p = nmv^2. \tag{6}$$

Since the kinetic energy of the molecules moving in the direction being considered is $\frac{1}{2}mv^2$ and since this energy is $\frac{1}{2}kT$,

$$p = nkT. \tag{7}$$

The pressure is proportional to both the gas concentration and to its temperature. This is the **perfect-gas law** applicable to ideal gases, in which particles do neither attract nor repel one another. Practical gases may not follow this law exactly owing to weak Van der Waals' forces between molecules and to the finite size of molecules (which causes the volume available to the gas to be smaller than the volume of the vessel containing it). The higher the concentration of the gas, the greater the error when using the perfect gas law. But in many situations the error tends to be small—the volume of air at 300 K and 100 kPa is overestimated by only 0.07%.

It proves convenient to count particles in terms of *kilomoles* (just as it might be useful to count loaves of bread in terms of *dozens*). While a dozen is equal 12, a kilomole is 6.022×10^{26}. This latter quantity is called **Avogadro's number,** N_0.[†]

Observe that $n = \mu N_0/V$ (μ is the number of kilomoles and V is the volume of the container).

$$p = \mu \frac{N_0 kT}{V} = \mu \frac{RT}{V}. \tag{8}$$

This is another form of the perfect gas law.

$$R \equiv kN_0 = 1.38 \times 10^{-23} \times 6.022 \times 10^{26} = 8314 \quad \text{J K}^{-1}\text{kmole}^{-1}. \tag{9}$$

R is the **gas constant**.

2.4 Internal Energy.

The total **internal energy**, U, of a gas is the sum of the energy of all molecules.

$$U \equiv \sum_i W_{mol_i} = \mu N_0 <W_{mol}> = \mu N_0 \frac{\nu}{2} kT = \mu \frac{\nu}{2} RT. \tag{10}$$

Thus, the internal energy, U, of a quantity, μ, of gas depends only on the temperature, T, and on the number, ν, of degrees of freedom of its constituent molecules.

2.5 Specific Heat at Constant Volume

When, in a fixed amount of gas, the temperature is changed, the internal energy also changes. When the volume is kept constant (as is the case of a mass of gas confined inside a rigid container), the rate of change of its internal energy with a change of temperature (per kilomole of gas) is called the **specific heat at constant volume**, c_v:

$$c_v = \frac{1}{\mu} \frac{dU}{dT} = \frac{\nu}{2} R. \tag{11}$$

[†] If Avogadro's number is taken as the number of molecules per mole (instead of kilomoles as one does when using the SI), then its value is 6.022×10^{23}.

Heat energy added to a gas is equally divided among the various degrees of freedom—hence the larger the number of degrees of freedom–the more energy is necessary to increase the energy of linear motion—that is, to increase the temperature. For this reason, the specific heats of a gas are proportional to ν.

We can see from Equation 11, that when a quantity μ of gas changes its temperature, then its internal energy changes by

$$\Delta U = \mu \int_{T_0}^{T} c_v dT. \tag{12}$$

Notice that we have left c_v inside the integral to cover the possibility that it may be temperature dependent, although this is not obvious from our derivations so far.

2.6 The First Law of Thermodynamics

Introduce an amount, Q, of heat energy into an otherwise adiabatic gas-filled cylinder equipped with a frictionless piston. **Adiabatic** means that no heat is exchanged between the gas in the cylinder and the environment. If the piston is allowed to move, it can do external work, W, by lifting a weight. If held immobile, no work will be done. In general, $W \neq Q$. In fact, since energy cannot be created from nothing, $W \leq Q$. What happens to the excess energy, $Q - W$?

The principle of conservation of energy requires that the internal energy of the system increase by just the correct amount. A "bookkeeping" equation is written:

$$\Delta U = Q - W, \tag{13}$$

where ΔU is the increase in internal energy. In differential form, the change in internal energy can be related to the incremental heat added and to the incremental work done by the system.

$$dU = dQ - dW. \tag{14}$$

Equations 13 and 14 are the mathematical statement of the **first law of thermodynamics**. It is a statement of conservation of energy. In all cases of interest here, the internal energy is the energy associated with the random motion—the **thermal** energy. A more complicated system may increase its internal energy through such additional mechanisms as atomic or molecular excitations, ionization, and others.

When heat is added at constant volume, there is no external work ($dW = 0$) and, consequently $dU = dQ$. Since the specific heat at constant volume is dU/dT (per kilomole),

$$\mu c_v = \frac{dU}{dT} = \frac{dQ}{dT}. \tag{15}$$

2.7 The Pressure-Volume Work

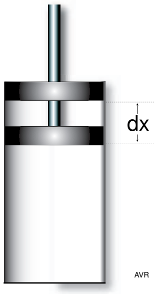

Figure 2.1 Cylinder with frictionless piston.

We mentioned, in the previous subsection, that work can be extracted from a closed cylinder-with-piston system. How much work is generated?

The force on the piston is pA, where A is the area of the piston face. If the piston moves a distance, dx, it does an amount of work:

$$dW = pAdx \tag{16}$$

The volume of the cylinder is changed by:

$$dV = Adx. \tag{17}$$

Thus,

$$dW = p\ dV \tag{18}$$

and

$$W = \int p\ dV. \tag{19}$$

2.8 Specific Heat at Constant Pressure

c_v is the amount of heat that has to be delivered to one kilomole of gas to increase its temperature by 1 K provided that the *volume* is kept unaltered. In a system like the one depicted in Figure 2.1, this corresponds to immobilizing the piston. On the other hand, if the *pressure* is kept constant, then, in order to increase the temperature by the same 1 K, more energy is needed. The extra energy is required because in addition to increasing the internal energy, heat must also do work lifting the piston. This work (per unit temperature rise) is pdV/dT, or

$$p\frac{dV}{dT} = p\frac{d}{dT}\ \frac{RT}{p} = R \tag{20}$$

because p is constant. It follows that

$$c_p = c_v + R = \frac{\nu}{2}R + R = \left(1 + \frac{\nu}{2}\right) R \qquad \text{J K}^{-1}\text{kmole}^{-1}. \tag{21}$$

The ratio of the two specific heats is

$$\gamma \equiv \frac{c_p}{c_v} = \frac{R(1+\nu/2)}{R\nu/2} = 1 + \frac{2}{\nu}. \tag{22}$$

2.9 Adiabatic Processes

In the closed system we have considered so far, we described the interplay between the internal energy, U, the work, W, and the heat, Q. The simplest possible system is one in which the cylinder is so well insulated that heat can neither enter nor leave. In such an **adiabatic** system, $\Delta Q = 0$. As the piston moves down, the work it does is entirely transformed into an increase in internal energy: $\Delta U = W$. The compression can be accomplished in a gradual manner so that at any given instant the pressure exerted by the piston is only infinitesimally larger than that of the gas—the compression is a succession of quasi-equilibrium states and the pressure is always uniform throughout the gas. Such is the case, for instance, when the piston is pressed down by the connecting rod of a mechanical heat engine, even though the action may appear to be very rapid. It is also possible to compress a gas abruptly as when an immobilized piston loaded with a heavy weight is suddenly released. In this case, the pressure of the gas immediately under the piston will rise rapidly but there is no time to transmit this change to the rest of the gas. A nonequilibrium situation is created. The former case—gradual compression—is by far the most common and most important. Nevertheless, we will consider first the abrupt compression, because gradual compression can be treated as an infinite succession of infinitely small abrupt steps.

2.9.1 Abrupt Compression

We will start with a qualitative description of what happens and then will examine an example.

Assume that a cylinder-and-piston system is in equilibrium. The piston, with a face area, A, is at a height, h_0 above the bottom of the cylinder enclosing a volume, $V_0 = h_0 A$. The force on the piston is F_0,[†] so that the pressure of the gas is $p_0 = F_0/A$. Next, the piston is clamped into place so that it cannot move and an additional mass is added to it. This increases the force to a value, F_1. At the very instant the piston is released, it will exert a pressure, $p_1 = F_1/A$, on the gas, but the latter is still at the substantially lower pressure, p_0. The piston will descend explosively to a height, h_1, and, after a while, will settle at a new height, h_1, when the gas pressure has risen to p_1. An amount of work, $W_{0\rightarrow 1} = F_1(h_0 - h_1)$ has

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[†] The force on the piston is the sum of the force exerted by the atmosphere plus the force owing to the weight of the piston.

been done on the gas and, owing to the adiabatic conditions, this work is entirely translated into an increase, $\Delta U = \mu c_v(T_1 - T_0)$, in internal energy. The compression caused a reduction in volume and an increase in pressure and temperature of the gas.

If next, the force on the piston is returned to its original value, $F_2 = F_0$, the piston will shoot up, and it is found that it will settle at a height, $h_2 > h_0$. The temperature will fall from the value, T_1, after the compression, to a new value, $T_2 > T_0$. The system does not return to its original state and the reason is obvious: The compression was caused by a force, F_1, but the expansion was against a smaller force, F_0. Thus, an amount of energy, $W_{0\to 1} - W_{1\to 2}$ was left over. This particular cycle extracted some energy from the environment. Hence, by definition, it is an irreversible process.

Example:

Consider the adiabatic cylinder-and-piston system shown in Figure 2.1. In our example, it contains $\mu = 40.09 \times 10^{-6}$ kilomoles of a gas whose $\gamma = 1.4$, independently of temperature. Its temperature is $T_0 = 300$ K. The cross-sectional area of the cylinder is $A = 0.001$ m^2.

The piston slides with no friction, exerting a force, $F_0 = 1000$ N. Consequently, the piston causes a pressure, $p_0 = \frac{F_0}{A} = \frac{1000}{0.001} = 10^6$ Pa.

The volume of the gas is

$$V_0 = \frac{\mu R T_0}{p} = \frac{40.09 \times 10^{-6} \times 8314 \times 300}{10^6} = 0.0001 \ \text{m}^3. \tag{23}$$

The piston hovers at $h_0 = V_0/A = 0.0001/0.001 = 0.1$ m above the bottom of the cylinder.

At equilibrium, the pressure of the gas is equal to the pressure the piston exerts. The specific heat at constant volume is

$$c_v = \frac{R}{\gamma - 1} = 20,785 \quad \text{J K}^{-1}\text{kmole}^{-1}. \tag{24}$$

The internal energy of the gas is

$$U_0 = \mu c_v T_0 = 40.09 \times 10^{-6} \times 20,785 \times 300 = 250 \quad \text{J}. \tag{25}$$

and the $p_0 V_0^{\gamma}$ product is

$$p_0 V_0^{\gamma} = 10^6 \times 0.0001^{1.4} = 2.51. \tag{26}$$

(continued)

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The fixed characteristics of the system are,

Area, $A = 0.001$ m ^{2},
Gas amount, $\mu = 40.09 \times 10^{-6}$ kmoles,
Gamma, $\gamma = 1.4$,
Specific heat at constant volume, c_v =20,785 JK^{-1}kmole^{-1},

and the initial data are

Force, $F_0 = 1000$ N,
Volume, $V_0 = 0.0001$ m^3,
Pressure, $p_0 = 10^6$ Pa,
Temperature, $T_0 = 300$ K,
Internal energy, $U_0 = 250$ J,
Height, $h_0 = 0.1$ m,
$p_0 V_0^\gamma = 2.51$.

Data on all the phases of this exercise are displayed in Table 2.1 at the end of the next subsection.

What happens if the force exerted by the piston is abruptly increased so that F_1 is now 10,000 N? The piston will go down stopping at a height, h_1. (Actually the piston will initially overshoot its mark and then oscillate up and down until the internal losses of the gas dampen out these oscillations.) When at equilibrium, the pressure of the gas is

$$p_1 = \frac{F_1}{A} = \frac{10,000}{0.001} = 10^7 \qquad \text{Pa.} \tag{27}$$

In moving from h_0 to h_1, the piston did an amount of work, $W_{0\to1}$,

$$W_{1\to2} = F_1(h_0 - h_1). \tag{28}$$

Since the cylinder is adiabatic, the internal energy of the gas must increase by an amount,

$$\Delta U_0 = \mu c_v (T_1 - T_0) = F_1(h_0 - h_1), \tag{29}$$

where T_1 is the temperature of the gas after compression. It is

$$T_1 = \frac{p_1 V_1}{\mu R} = \frac{p_1 A h_1}{\mu R} = \frac{F_1}{\mu R} h_1. \tag{30}$$

Introducing Equation 30 into Equation 29,

$$F_1(h_0 - h_1) = \frac{c_v}{R} F_1 h_1 - \mu c_v T_0. \tag{31}$$

(continued)

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Solving for h_1,

$$h_1 = \frac{\gamma - 1}{\gamma}\left(h_0 + \mu c_v \frac{T_0}{F_1}\right) \tag{32}$$

Using the values of the example, $h_1 = 0.0357$ m.

The volume of the gas is now

$$V_1 = Ah_1 = 0.001 \times 0.0357 = 35.7 \times 10^{-6} \quad \text{m}^3. \tag{33}$$

The gas temperature is

$$T_1 = \frac{p_1 V_1}{\mu R} = \frac{10^7 \times 35.7 \times 10^{-6}}{40.09 \times 10^{-6} \times 8314} = 1071.4 \quad \text{K}. \tag{34}$$

and the pV^γ product is

$$p_1 V_1^\gamma = 10^7 \times (35.7 \times 10^{-6})^{1.4} = 5.94. \tag{35}$$

Collecting these data, we obtain the following values after the abrupt compression:

$F_1 = 10,000$ N,
Volume, $V_1 = 35.7 \times 10^{-6}$ m^3,
Pressure, $p_1 = 10^7$ Pa,
Temperature, $T_1 = 1071.4$ K,
Height, $h_1 = 0.0357$ m,
$p_1 V_1^\gamma = 5.94$.

The amount of energy the piston delivered to the gas is

$$W_{0\to 1} = F_1(h_0 - h_1) = 10,000(0.1 - 0.0357) = 643 \quad \text{J}. \tag{36}$$

In this example, the sudden application of 10,000 N (an increase of 9,000 N) resulted in a strongly nonequilibrium situation. At the moment this additional force was applied, the piston exerted a pressure of 10^7 Pa while the opposing pressure of the gas was only 10^6 Pa. The piston descended explosively seeking a new equilibrium. We will attempt to reverse the situation, starting with the values above, also listed in the second column (“abrupt compression”) of Table 2.1. We suddenly remove 9,000 N (leaving the 1,000 N we had originally). Calculations entirely parallel to the one we just did would lead to the new final values below:

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$F_2 = 1,000$ N.
Volume, $V_2 = 268 \times 10^{-6}$ m^3.
Pressure, $p_2 = 10^6$ Pa.
Temperature $T_2 = 795.6$ K.
Height $h_2 = 0.265$ m.
$p_2 V_2^{\gamma} = 9.98$.

The force on top of the piston is back to its original value of 1,000 N, but the state of the gas is very far from that at the beginning of the experiment. This, as we pointed out, is to be expected. We compressed the gas with a 10,000 N force and then lifted the piston against a much smaller 1,000 N force. Although the final height is larger than it was initially, some energy is left over. Indeed, the internal energy of the gas is now $U_2 = \mu c_v T_2 = 663$ J, an increase of 413 J over the initial value of $U_0 = 250$ J. This is, of course, the difference between the mechanical input energy, $W_{0\rightarrow 1}$ and the mechanical output energy, $W_{1\rightarrow 2}$.

2.9.2 Gradual compression

Can a gas be compressed adiabatically in such a way that when expanded it returns exactly to the same state? In other words, can an adiabatic compression be reversible? The answer is yes, provided the force is applied gradually. The compression (or expansion) must proceed in a number of steps each of which maintains the gas in quasi-equilibrium. This can be demonstrated numerically in a simple way by using a spread sheet such as Excel.

Starting with the conditions we had at the beginning of the experiment, increment the force by a small amount, ΔF, so that $F_i = F_{i-1} + \Delta F$. Calculate h_i from

$$h_i = \frac{\gamma - 1}{\gamma} \left(h_{i-1} + \mu c_v \frac{T_{i-1}}{F_i} \right). \tag{37}$$

Calculate T_i from

$$T_i = \frac{F_1 h_i}{\mu R}. \tag{38}$$

Iterate until $F_i = F_{final}$. Here, F_{final}(10,000 N, in this example) is the final value of the force.

For sufficiently small ΔF, it is found that $h_{final} = 0.0193$ m and $T_{final} = 579.2$ K. It is also found that if we decompress in the same manner, we return to the original values of h, V, and T. The process is reversible.

2.10

In addition, it turns out that the final value of pV^γ is the same as the initial one. Indeed, pV^γ is the same in all steps of the calculation. This is not a coincidence. Later on in this chapter, we will demonstrate that in a reversible adiabatic process, pV^γ is constant. In Chapter 4 we will demonstrate that this so called **polytropic law** applies to all **isentropic processes**. The use of the polytropic law allows the calculation of reversible adiabatic processes in a simple way, not requiring the iteration technique mentioned above.

The results of the reversible compression are listed below:

Volume, $V_{reversible} = 19.3 \times 10^{-6}$ m^3.
Pressure, $p_{reversible} = 10^7$ Pa.
Temperature $T_{reversible} = 579.2$ K.
Height $h_{reversible} = 0.0193$ m.
$(pV^\gamma)_{reversible} = 2.51$.
$F_{reversible} = 10,000$ N.

Table 2.1
Variables in Different Phases of the Compression Experiment

Phase	Subscript	Vol. liters	Press. MPa	Temp. K	Height cm	pV^γ	Force N
Initial	"0"	100	1	300	10	2.51	1,000
Abrupt compression	"a"	35.7	10	1071	3.57	5.94	10,000
Abrupt expansion	"$a_{\ rever.}$"	265	1	796	26.5	9.98	1,000
Gradual compression	"$_{reversible}$"	19.3	10	579	1.93	2.51	10,000

2.9.3 p-V Diagrams

It is easier to understand the process by plotting the pressure versus volume behavior of the gas as illustrated in Figure 2.2.

Since reversible compression is the result of a large number of succeeding equilibrium steps, we can calculate the pressure and volume after each step. This is indicated by the smooth (exponential looking) curve in the figure. Notice that the shaded area under the curve represents the amount of work done during the compression.

The compression in the experiment starts from 1 MPa (when the gas volume was 100 liters) and ends when the pressure reaches 10 MPa (at a volume of 19.3 liters).

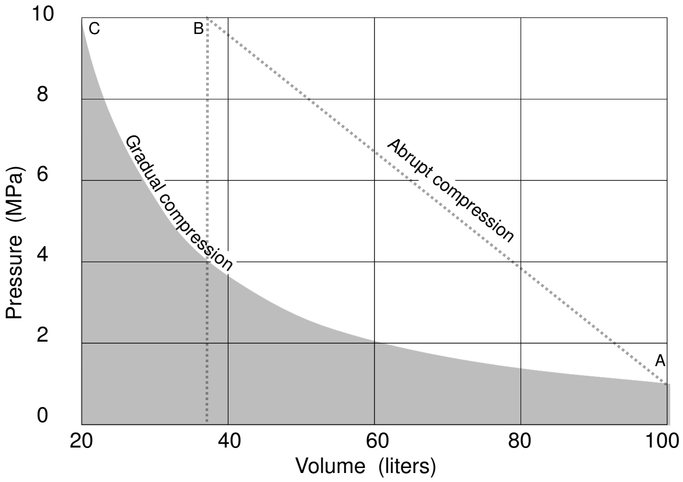

Figure 2.2 For a reversible adiabatic compression, the progression from the initial state, A, to the final state, C, is smooth and predictable. For an abrupt compression, it is impossible to specify the path of the gas.

In the case of the abrupt compression, the initial state, (A), is the same as in the previous case. The final state, (B), has the same pressure (10 MPa) as before but, since the gas is at a higher temperature, the volume is larger (35.7 liters versus 19.3 liters). However, the path from one state to the other is unknown, a fact indicated by the dotted line. During such a rapid compression, the pressure and the temperature cannot be specified because they are not uniform throughout the mass of the gas. As the piston presses down, the gas piles up in the vicinity of the piston, not having time to spread out uniformly.

The terms "gradual" and "abrupt" are relative. In most machines, even at high speed operation, the compression (or expansion) can be taken (with little error) as gradual.

2.9.4 Polytropic Law

Assume that the cylinder with piston used in our discussion of the pressure-volume work is insulated so that no heat can be exchanged between the gas inside and the environment outside. We have adiabatic conditions, and the heat exchanged is

$$dQ = 0. \tag{39}$$

Consider an infinitesimal step in the compression process. The work is

$$dW = p\,dV \tag{40}$$

From the first law of thermodynamics, we have

$$dQ = dU + dW = 0, \tag{41}$$

and from the perfect gas law,

$$p = \mu \frac{RT}{V}. \tag{42}$$

It follows that

$$dW = \mu RT \frac{dV}{V} \tag{43}$$

and

$$dU = \mu c_v dT, \tag{44}$$

$$\mu c_v \frac{dT}{T} + \mu R \frac{dV}{V} = 0, \tag{45}$$

$$c_v \ln T + R \ln V = constant. \tag{46}$$

But $R = c_p - c_v$, hence

$$\ln T + (\gamma - 1) \ln V = constant, \tag{47}$$

$$T\ V^{\gamma - 1} = constant. \tag{48}$$

Since $pV = \mu RT$,

$$pV^{\gamma} = constant. \tag{49}$$

This is called the **polytropic** law and is the characteristic of a reversible adiabatic compression or expansion.

2.10 Isothermal Processes

In the previous sub-section, we discussed a particularly important thermodynamic transformation—the adiabatic process. We will now examine another equally important transformation—the isothermal process.

Under all circumstances, the work done when a gas expands from volume V_0 to V_1 (see the Section 2.7) is,

$$W_{0,1} = \int_{V_0}^{V_1} p dV. \tag{50}$$

Under isothermal conditions,

$$pV = p_o V_0 \qquad \therefore \qquad p = p_o \frac{V_0}{V} \tag{51}$$

$$W_{0,1} = p_0 V_0 \int_{V_0}^{V_1} \frac{dV}{V} = p_0 V_0 \ln \frac{V_1}{V_0} = p_0 V_0 \ln \frac{p_0}{p_1} = \mu RT \ln \frac{p_0}{p_1}. \tag{52}$$

We will re-derive this result using a more detailed procedure[†] in the hope that this will bring out more clearly the basic underlying mechanism of the process.

Assume that the cylinder is no longer thermally insulated; it is in thermal contact with a bath maintained at a constant 300 K. The frictionless piston is held in place by a weight, so that the initial pressure is p_0. We want to know how much energy can be extracted by allowing the expansion of the gas to a final pressure, p_f. This requires removing some weight from the piston. We assume that there is no outside atmospheric pressure.

Imagine the original weight had a mass of 10 kg and that, suddenly, 9 kg are removed. The piston will shoot up lifting 1 kg. Since there is no friction, the system oscillates, damped only by the internal dissipation of the gas which, cooled by expansion, warms up again as heat from the bath is conducted in. After a new equilibrium is established, a mass of 1 kg will have been lifted by, say, 1 meter. The work done is $W = mgh = 1 \times 9.8 \times 1 = 9.8$ J. Although the final temperature is the same as the initial one, *the processes is not isothermal*, because during the expansion the temperature first decreased and then rose to its original value. If isothermal, the temperature must not change throughout the whole process.

Let us rerun the experiment leaving this time 2 kg on the piston. The mass will rise and the oscillations will eventually settle down. Now an additional 1 kg is removed and the process repeats itself. The final state is the same as in the first experiment, but the work done is now $2 \times 9.8 \times 0.444 + 1 \times 9.8 \times 0.556 = 14.2$ J because the mass was raised 0.444 m in the first step (see Problem 2.3). The obvious reason for this larger amount of work is that, although only 1 kg reached the 1 m height, a total of 2 kg was lifted part of the way.

Maximum work is done by using an infinite number of steps, each one removing infinitesimally small amounts of mass. Under such circumstances, the expansion is isothermal because heat from the bath flows into the gas after each infinitesimal cooling, thus keeping the temperature at a constant 300 K. What is this maximum work?

Define a decompression ratio, r

$$r \equiv \frac{p_0}{p_f}. \tag{53}$$

Let the decompression proceed by (geometrically) uniform steps and let n be the number of steps. Then,

$$r^{1/n} = \frac{p_{i-1}}{p_i}. \tag{54}$$

The work done in step i is

$$W_i = (h_i - h_{i-1})F_i \tag{55}$$

[†] Suggested by Prof. D. Baganoff of Stanford University.

where F_i is the weight lifted in step i and is

$$F_i = p_i A, \tag{56}$$

A being the area of the piston.

The height reached by the weight after step i is

$$h_i = \frac{V_i}{A}, \tag{57}$$

hence,

$$W_i = \frac{V_i - V_{i-i}}{A} p_i A = V_i p_i - V_{i-1} p_i = V_0 p_0 - V_{i-1} p_i, \tag{58}$$

because after each step the temperature is returned to its original value, T_0, and consequently $pV = p_0 V_0$.

$$W_i = V_0 p_0 \left(1 - \frac{p_i}{p_{i-1}}\right) = V_0 p_0 \left(1 - r^{-1/n}\right). \tag{59}$$

The total work is

$$W = V_0 p_0 \sum_{i=1}^{n} \left(1 - r^{-1/n}\right) = V_0 p_0 n \left(1 - r^{-1/n}\right), \tag{60}$$

$$W = V_0 p_0 \ln r. \tag{61}$$

This is the formula derived earlier. An expanding mass of gas does maximum work when the expansion is isothermal.

2.11 Functions of State

The **state** of a given amount of perfect gas is completely defined by specifying any two of the following three variables: pressure, volume, or temperature. The third variable can be derived from the other two (if the number of kilomoles of the gas is known) by applying the perfect gas law.

When a gas changes from one state to another, it is possible to calculate the change in its internal energy. To do this, it is sufficient to know the amount of gas, its specific heat at constant volume and the initial and final temperatures. It is completely irrelevant what intermediate temperatures occurred during the change.

On the other hand, to calculate the amount of work done during a change of state, it is necessary to know exactly which way the change took place. Knowledge of the initial and final states is not sufficient. In the experiment described in the preceding subsection, the work to achieve the final state depended on the which way the mass was raised. One cannot tell how much work is required to go from one state to another just by knowing what these states are. If one sees a person on the top of a hill, one cannot know how much effort was made to climb it. The person may have taken an easy, paved path or may have traveled a longer, boulder strewn route. In other words, energy is **not** a function of the state of gas.

2.12 Enthalpy

So far we have considered only **closed systems** in which a fixed mass of gas is involved. Many devices, such as a turbine, are **open systems** involving a flow of gas. Instead of fixing our attention on a given mass of gas, we must consider a given volume through which a fluid flows suffering some thermodynamic transformation. In order to quantify the changes in energy in such an open system, one must account for the energy that the fluid brings into the system and removes from it.

To force the flow of the fluid into the open system depicted in the Figure 2.3, imagine a (fictitious) piston exerting a pressure, p, to press a volume, V, of gas into the device. The piston exerts a force, pA, and, to push the gas a distance, L, uses an energy, $pAL = pV$. The flow of energy into the device is $p_{in}V_{in}$. Exiting, the gas carries an energy, $p_{out}V_{out}$. The net energy deposited by the flow is $p_{in}V_{in} - p_{out}V_{out}$. If the gas also changed its internal energy, then the total work that the device generates is

$$W = \Delta(pV) + \Delta U = \Delta(pV + U) \equiv \Delta H. \qquad (62)$$

This assumes that the device is adiabatic (heat is not exchanged with the environment through the walls).

The combination, $pV + U$, occurs frequently in thermodynamics and it becomes convenient to define a quantity, called **enthalpy**,

$$H \equiv U + pV. \qquad (63)$$

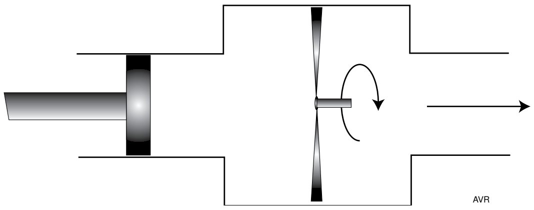

Figure 2.3 An open system in which the flow of gas does some work.

H, U, and pV, being energies, are relative—that is, they must be referred to some arbitrary level. Their magnitudes are of little importance; what is of interest is their *change*:

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + p\Delta V + V\Delta p. \tag{64}$$

At constant pressure, ΔH is simply $\Delta U + p\Delta V$ and is therefore equal to the heat, ΔQ, added to the system:

$$\Delta H = \Delta U + W = \Delta Q \qquad \text{(at constant pressure).} \tag{65}$$

For this reason, enthalpy is sometimes called the **heat content**. It is a quantity commonly used by chemists because reactions are frequently carried out in open vessels, i.e., at constant pressure.

From Equation 12 (per kilomole)

$$\Delta U = \int_{T_0}^{T} c_v dT. \tag{66}$$

Using the perfect gas law (again, per kilomole), and Equation 64,

$$\begin{aligned}\Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta(RT) &= \int_{T_0}^{T} c_v dT + R\int_{T_0}^{T} dT \\ &= \int_{T_0}^{T} (c_v + R) dT = \int_{T_0}^{T} c_p dT \qquad (67)\end{aligned}$$

Compare Equations 66 and 67.

2.13 Degrees of Freedom

The formulas we developed for the specific heats and for their ratio, γ, require knowledge of the number of degrees of freedom, ν, of the molecules. From our derivation, this number should be an integer and it should be independent of temperature. What do experimental data have to say?

Consider monatomic gases whose molecules have three translational degrees of freedom. If this were all, their γ would be exactly $1+2/3 = 1.667$ (Equation 22). Table 2.2 shows that the measured value of γ for helium, argon and krypton is *approximately* (but not exactly) the expected one. However, since the molecules of these gases have some volume, they must be able to spin. At least one additional degree of freedom must be assigned to this spin motion, and ν should not be smaller than 4. This would lead to a γ of $1 + 2/4 = 1.5$, a value significantly below the observed one.

Take now the diatomic molecule, H_2. It should have 3 translational and 2 rotational degrees of freedom. In addition, it can vibrate which should contribute another 2 degrees of freedom (one for the kinetic energy of vibration and one for the potential). Thus, the total number of degrees of freedom should be at least 7 and the value of γ should be $1+2/7 = 1.286$.

At 2300 K, hydrogen does have a γ of 1.3—corresponding to a $\nu = 6.67$, and as can be seen from Figure 2.4, it appears that at even higher temperature, the number of degrees of freedom might reach 7. At very low temperatures, ν tends toward 3 and H_2 behaves as a pointlike monatomic molecule.

Between these temperature extremes, ν, varies smoothly, assuming fractional, non-integer, values. Clearly, any single molecule can only have an integer number of degrees of freedom, but a gas, consisting of a large collection of molecules, can have an *average* ν that is fractional. At any given temperature, some molecules exercise a small number of degrees of freedom, while others exercise a larger one. In other words, the principle of equipartition of energy (which requires equal energy for all degrees of freedom of all molecules) breaks down. Thus, for real gases, the specific heats and their ratio, γ, are temperature dependent, although not extremely so. See the graphs in "Free Energy Dependence on Temperature" in Appendix A to the chapter on fuel cells.

For some estimates it is sufficient to assume that these quantities are constant. One can assume $\nu = 5$ for H_2 and O_2, and $\nu = 7$ for the more complicated molecule H_2O, all at ambient temperature. More precise calculations require looking up these values in tables. See, for instance, a listing of observed values of c_p and of γ for H_2, O_2, and H_2O in the table in Appendix A mentioned.

Some general trends should be remembered: More complex molecules or higher temperatures lead to a larger number of degrees of freedom and consequently larger specific heats and smaller γ.

Table 2.2
Ratio of the Specific Heats of Some Monatomic Gases

Gas	Temp. (K)	γ
Helium	93	1.660
Argon	298	1.668
Krypton	298	1.68

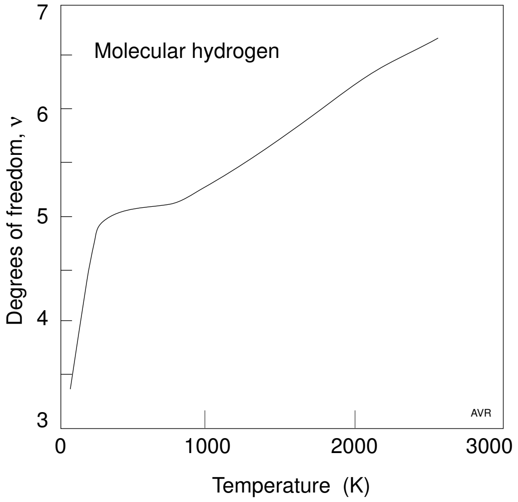

Figure 2.4 The number of degrees of freedom of molecular hydrogen as a function of temperature.

2.14 Entropy

When one considers different forms of energy, one can intuitively rank them in order of their "nobility." Electric energy must be quite "noble"—it can easily be transformed into any other kind of energy. The same is true of mechanical energy because it can (theoretically) be transformed into electricity and vice-versa without losses. Heat, however, must be "degraded" energy—it is well known that it cannot be entirely transformed into either electric or mechanical energy (unless it is working against a heat sink at absolute zero). It turns out that chemical energy has a degree of "nobility" lower than that of electricity, but higher than that of heat.

Still, intuitively, one can feel that the higher the temperature, the higher the corresponding "nobility" of the heat—that is, the more efficiently it can be transformed into some other form of energy.

Let us try to put these loose concepts on a more quantitative basis.

Consider two large adiabatic reservoirs of heat: one (which we shall call the source) at a temperature, T_H, and one (the sink) at a lower temperature, T_C. The reservoirs are interconnected by a slender metal rod forming a thermally conducting path between them. We shall assume that, for the duration of the experiment, the heat transferred from source to sink is much smaller than the energy stored in the reservoirs. Under such circumstances, the temperatures will remain unaltered.

Assume also that the rod makes thermal contact with the reservoirs but not with the environment. The amount of heat that leaves the source must, then, be exactly the same as that which arrives at the sink. Nevertheless, the heat loses part of its "nobility" because its arrival temperature is lower than that at the departure. "Nobility" is lost in the conduction process.

Form the Q/T ratio at both heat source and at the heat sink. Q is the amount of heat transferred. Clearly, $Q/T_H < Q/T_C$. We could use this ratio as a measure of "ignobility" (lack of "nobility"), or, alternately, the ratio $-Q/T$ as a measure of "nobility." Loosely, **entropy** is what we called "ignobility":

$$S \equiv \frac{Q}{T}. \tag{68}$$

It is important to realize that in the above experiment, energy was conserved but "nobility" was lost; it did not disappear from the experimental system to emerge in some other part of the universe—it was lost to the universe as a whole. There is no law of conservation of "ignobility" or entropy. In any closed system, at best, the entropy will not change, but if it does, it always increases.† This is a statement of the **second law of thermodynamics**.

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† However, a given system does not always tend toward maximum randomness. Systems may spontaneously create complicated structures such as life forms emerging from some primeval soup.

Since there is no heat associated with electric or mechanical energy, these forms have zero entropy.

We have seen that entropy is a measure of both the *quality* of heat and of the randomness of an arrangement. The higher the temperature associated with a quantity, Q, of heat, the lower the corresponding entropy, Q/T. On the other hand, the higher the temperature of a gas, the higher the randomness of its molecules—hence the higher its entropy. To resolve this apparent paradox, consider an amount of heat, Q_{in}, flowing, at temperature, T_{in}, into a volume of gas otherwise adiabatic. We have an input into the gas of both energy and entropy. Clearly, the increase in energy causes the gas temperature to rise, and, at the same time, the incoming entropy causes an increase in the entropy of the gas, because, although entropy is not conserved, it cannot, under the second law of thermodynamics, simply disappear. Hence raising the temperature of the gas also raised its entropy.

2.14.1 Changes in Entropy

Returning to the question of functions of state, it is important to know that entropy is such a function. To determine the change in entropy in any process, it is sufficient to determine the entropies of the final and the initial states and to form the difference.

Some processes can drive a system through a full cycle of changes (pressure, volume and temperature) in such a way that, when the cycle is complete, the system is returned to the initial state. Such processes are **reversible**. To be reversible, the net heat and the net work exchanged with the environment must be zero. In any reversible process, the change in entropy of a substance owing to a change from State “1” to State “2” is

$$\Delta S = \int_{\text{“1”}}^{\text{“2”}} \frac{dQ}{T} \tag{69}$$

Here, S is the entropy and ΔS is the change in entropy.

In an **adiabatic** processes, $dQ = 0$. Hence

$$S = constant. \tag{70}$$

In an **isothermal** process, $\Delta S = Q/T$ because T is constant. Notice, however, that according to the first law of thermodynamics, $\Delta U = Q - W$, but, in an isothermal change, $\Delta U = 0$—hence $W = Q$ and, since in such a change, $W = p_0 V_0 \ln p_1/p_2$,

$$\Delta S = \frac{V_0 p_0}{T} \ln \frac{p_1}{p_2} = \mu R \ln \frac{p_1}{p_2}. \tag{71}$$

In an **isobaric** process,

$$\Delta S = \mu \int_{\text{“1”}}^{\text{“2”}} c_p \frac{dT}{T} \tag{72}$$

and, if c_p is constant,

$$\Delta S = \mu c_p \ln \frac{T_2}{T_1}. \tag{73}$$

In an **isometric** process,

$$\Delta S = \mu \int_{\text{“1”}}^{\text{“2”}} c_v \frac{dT}{T} \tag{74}$$

and if c_v is constant,

$$\Delta S = \mu c_v \ln \frac{T_2}{T_1}. \tag{75}$$

The change in entropy of μ kilomoles of a substance owing to an isobaric change of phase is

$$\Delta S = \mu \frac{Q_L}{T}, \tag{76}$$

where Q_L is the **latent heat of phase change** (per kilomole) and T is the temperature at which the change takes place.

Collecting all these results:

Table 2.3

Changes in Entropy

Process	ΔS	Equation
Adiabatic	zero	(70)
Isothermal	$\mu R \ln \frac{p_1}{p_2}$	(71)
Isobaric	$\mu \int_{\text{“1”}}^{\text{“2”}} c_p \frac{dT}{T}$	(72)
Isobaric (const. c_p)	$\mu c_p \ln \frac{T_2}{T_1}$	(73)
Isometric	$\mu \int_{\text{“1”}}^{\text{“2”}} c_v \frac{dT}{T}$	(74)
Isometric (const. c_v)	$\mu c_v \ln \frac{T_2}{T_1}$	(75)
Phase change	$\mu \frac{Q_L}{T}$	(76)

2.15 Reversibility

In the experiment of Section 2.14, it is impossible to reverse the direction of heat flow without a gross change in the relative temperatures, T_H and T_C. It is an **irreversible** process.

Let us examine another case (suggested by professor D. Baganoff of Stanford University) designed to illustrate reversibility:

Consider again an adiabatic cylinder with a frictionless piston. It contains 10 m^3 of an ideal monatomic gas ($\gamma = 1.67$) under a pressure of 100 kPa at 300 K. We will follow the behavior of the gas during compression and subsequent expansion by means of the p versus V and the T versus V diagrams in Figure 2.5. The initial state is indicated by "1" in both graphs.

When the piston is moved so as to reduce the volume to 2 m^3, the pressure will rise along the adiabatic line in such a way that the pV^γ product remains constant. When State "2" is reached, the pressure will have risen to 1470 kPa and the temperature to 882 K. The work done during the compression is $\int pdV$ between the two states and is proportional to the area under the curve between "1" and "2."

If the piston is allowed to return to its initial position, the gas will expand and cool, returning to the initial state, "1." The process is completely reversible. Now assume that inside the cylinder there is a solid object with a heat capacity equal to that of the gas. If we compress the gas rapidly and immediately expand it, there is no time for heat to be exchanged between the gas and the solid which will remain at its original temperature of 300 K. The process is still reversible.

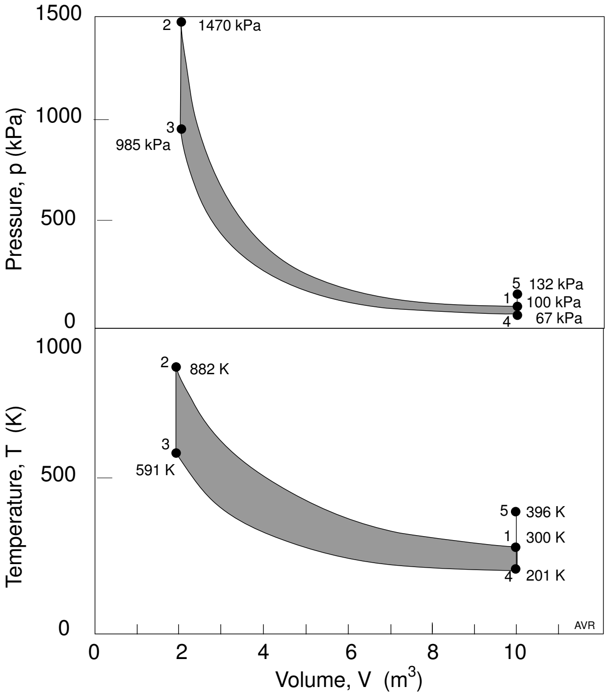

Figure 2.5 Pressure-volume and temperature-volume diagrams for the experiment described in the text.

2.22

However, if one compresses the gas and then waits until thermal equilibrium is established, then half of the heat generated will be transferred to the solid and the gas will cool to $(882 + 300)/2 = 591$ K, while its pressure falls to 985 kPa according to the perfect gas law. This is State "3."

When the gas expands again to 10 m^3, it cools down to 201 K and the pressure falls to 67 kPa (State "4"). Immediately after this expansion, the solid will be at 591 K. Later, some of its heat will have been transferred back to the gas whose temperature rises to 396 K and the pressure will reach 132 kPa ("5"). The gas was carried through a full cycle but did not return to its initial state: its temperature (and internal energy) is now higher than initially. The increase in internal energy must be equal to the work done on the gas (i.e., it must be proportional to the shaded area in the upper portion of Figure 2.5 which is equal to the area under curve "1" to "2" minus that under curve "3" to "4." The process is irreversible.

What happens if the compression and the expansion are carried out infinitely slowly? Does the process become reversible? You will find that it does when you do Problem 2.2. An electric analogy may clarify the situation. When a real battery (represented by a voltage source, V, with a an internal resistance R) is used to charge an ideal energy accumulator, part of its energy will dissipate as heat through the internal I^2R losses, leaving only part to reach the accumulator. Clearly, the relative loss decreases as the current decreases—that is, as the charge time increases. If the energy is transferred from the battery to the accumulator infinitely slowly ($I \rightarrow 0$) there are no losses. The system is reversible in the sense that all the energy transferred to the accumulator can later be returned to the battery.

2.15.1 Causes of Irreversibility

Among the different phenomena that cause thermodynamic processes to become irreversible one can list:

2.15.1.1 Friction

Of all the causes of irreversibilities, friction is perhaps the most obvious. For example, in the cylinder-piston case, if some energy is lost by friction during compression, it is not returned during expansion; on the contrary, additional losses occur during this latter phase.

2.15.1.2 Heat Transfer Across Temperature Differences

Consider a metallic wall separating a source of heat—say a flame—from the input of a heat engine. All the heat, Q, absorbed from source is transmitted without loss through the wall, yet for this heat to flow there must be a temperature difference across the wall. The source side is at T_1, the engine side is at T_2, and T_1 must be larger than T_2. The entropy on the source side is Q/T_1 and on the engine side is Q/T_2, which is, of course larger than Q/T_1. So, in passing through the wall, the entropy was increased—the heat became less "noble" on the engine side.

In Chapter 3, we will show that the maximum efficiency of a heat engine is $\eta = \frac{T_H - T_C}{T_H}$. If the engine could have operated without the wall, its efficiency could have reached $\frac{T_1 - T_C}{T_1}$ and would be larger than when operated on the other side of the wall when it would be limited to $\frac{T_2 - T_C}{T_2}$.

2.15.1.3 Unrestrained Compression or Expansion of a Gas

In the subsection on adiabatic processes, we dealt with an example of abrupt expansion of a gas and found that it led to irreversibilities.

2.16 Negentropy

We have stressed that energy cannot be consumed. The conservation of energy is one of the laws of nature. When we use energy, we degrade it, so all energy we use is eventually degraded to heat and, one hopes, is radiated out into space in the form of long-wave infrared radiation.

Consider an example. An engine produces energy by extracting heat from the warm surface waters of the ocean (at some 300 K) and rejecting a smaller amount of heat to the cold waters near the bottom at, say, 275 K. All energy produced is used to compress adiabatically 10,000 kilomoles of a gas from 10^5 to 10^7 pascals (from about 1 to 100 atmospheres). If the initial temperature of the gas was 300 K, what is its final temperature?

Let p_0 and p_H be, respectively, the initial and the final pressures, and T_0 and T_H be the corresponding temperatures. Then,

$$\frac{T_H}{T_0} = \left(\frac{p_H}{p_0}\right)^{\frac{\gamma-1}{\gamma}}, \tag{77}$$

where γ is taken, in this example, as 1.4 (equivalent to 5 degrees of freedom). The corresponding specific heat at constant volume is 20.8 kJ $\text{K}^{-1}\text{kmole}^{-1}$.

For a 100:1 adiabatic compression, the temperature ratio is 3.7, and the T_H will be $3.7 \times 300 = 1110$ K. After compression, the volume is

$$V_H = \mu \frac{RT_H}{p_H} = 10,000 \frac{8314 \times 1110}{10^7} = 9230 \text{ m}^3. \tag{78}$$

The work required for such a compression is

$$W = 20.8 \times 10^3 \times 10000 \times (1110 - 300) = 168 \text{ GJ}. \tag{79}$$

Let the gas cool to 300 K—the temperature of the ocean surface. All the thermal energy (168 GJ) is returned to the waters. If the canister with gas is towed to the beach, we will have not removed any energy from the ocean, yet we will have 10,000 kilomoles of gas at a pressure of

$$p = \mu \frac{RT}{V} = 10,000 \frac{8314 \times 300}{9230} = 2.7 \text{ MPa}. \tag{80}$$

The internal energy of the compressed gas is no larger than that of an equal amount of the gas at the same temperature but at a much lower pressure; the internal energy is independent of pressure. Let the gas expand through a 100% efficient turbine, allowing its pressure to fall to 10^5 Pa. The work done by the turbine must come from the internal energy of the gas; this means that the gas must cool down. The temperature ratio (Equation 77) will be 2.56. Thus the gas exhausted from the turbine will be at 117 K.

The energy delivered by the turbine to its load is

$$W = 20.8 \times 10,000 \times (300 - 117) = 38 \text{ GJ}. \tag{81}$$

We have "generated" 38 GJ that certainly did not come from the ocean. Where did it come from? It came from the gas itself that had its internal energy reduced by cooling to 117 K. Actually, it came from the ambient air that was itself cooled by the exhaust from the turbine. The work delivered by the turbine will eventually be degraded to "waste" heat, reheating the environment by exactly the same amount it was cooled. Thus, in this whole process, energy was conserved, but we were able to perform useful work (the generator output) by removing something from the ocean. What was it?

What we did was to randomize the ocean by mixing cold bottom water with warm surface water. More precisely, we increased the entropy of the ocean. The canister carried away a certain amount of **negentropy**. Here we used the semantically more acceptable concept of **negative entropy**, a quantity that can be consumed. Marchetti (1976), who coined the word "negentropy," proposed the system just described as a method for "supplying energy without consuming energy." This is, of course, what is done in all cases in which energy is utilized. Although the system is technically feasible, it is commercially unattractive because the canister has but a small negentropy-carrying capacity compared with the large requirements of material for its construction. The main point to be learned from this example is that the consumable is negentropy, not energy.

2.17 How to Plot Statistics

The World Almanac lists the U.S. population distribution by age (for 1977) in the following manner:

Table 2.4
U.S. Population Distribution by Age

Age Interval years	Number of People millions
Under 5	15.2
5–13	32.2
14–17	16.8
18–20	12.8
21–44	72.0
45–64	43.8
65 and over	23.5

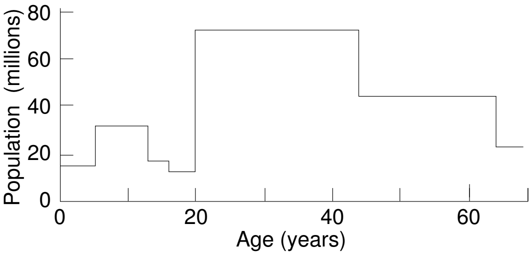

Figure 2.6 Inappropriate way of plotting population versus age. The area under the plot does not have the dimension of number of people.

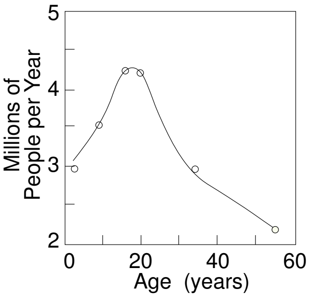

Figure 2.7 Number of people plotted in 1-year age interval.

Table 2.5
U.S. Population Distribution by Age

Age Interval (years)	Mean Age (years)	Age Interval (years)	Number of people (millions)	(people/year)
0–5	2.5	5	15.3	3.07
5–3	9.5	9	32.2	3.58
14–17	16	4	16.8	4.20
18–20	19,5	3	12.8	4.26
21–44	33.0	24	72.0	3.00
45–64	55.0	20	43.8	2.19
over 64	?	?	23.5	—

In search of a meaningful way of graphically presenting the data above, one can build the histogram shown in Figure 2.6. However, owing to the disparate age intervals chosen in tabulating the data, the histogram is not very enlightening. It would be better to use uniform age intervals—the smaller, the better. In the limit, the best would be to plot $\partial N/\partial A$ versus A. where N is the number of people and A is the age. To do this, we will have to construct another table, derived from the data in Table 2.4.

The data in the last column of Table 2.5 are plotted in Figure 2.7. A continuous line joined the data points. The area under the resulting curve is proportional to the population of the country. In illustrating the energy distribution of, for instance, gas molecules, it is informative to present plots of $\partial N/\partial W$ versus W or versus v (either energy or velocity) but not a plot of N versus W, as one is sometimes tempted to do.

2.18 Maxwellian Distribution

If molecules have a uniform velocity distribution, how many molecules have velocities less than a given value $|v|$? To answer this question, let us remember that at any time, each molecule is at some position (x, y, z)

and has some velocity (v_x, v_y, v_z). As far as the energy in the gas is concerned, the exact position of the molecules is irrelevant but their velocity is not. Although the individual velocities are changing all the time, in a gas at constant temperature, any instant in time is statistically equivalent to any other. In other words, any instantaneous picture of the velocities is adequate to describe the statistical behavior of the gas.

Let us plot the velocities of the molecules in a system of orthogonal coordinates, v_x, v_y, and v_z—that is, in **velocity space**. Alternatively, we could plot the momenta, mv_x, mv_y, and mv_z, in the **momentum space**. Since we are assuming that molecules have uniform velocity (or momentum) distribution, the velocity (or the momentum) space is uniformly populated. Thus, the number of molecules that have less than a certain velocity, $|v|$, is proportional to the volume of a sphere of radius v (or p) in the space considered. This means that the number of molecules with velocity less than $|v|$ (or momenta less than $|p|$) must be proportional to v^3 (or p^3). Hence, the number of molecules with velocity between v and $v + dv$ (momenta between p and $p + dp$) must be proportional to $\partial v^3/\partial v$, i.e., to v^2 (or p^2).

In real systems, uniform velocity distribution is unusual. In common gases, a distribution that fits experimental observation is one in which the probability, f, of finding a molecule with a given energy, W, is

$$f = \exp\left(-\frac{W}{kT}\right). \tag{82}$$

Under such conditions, the number of molecules with velocities between v and $v + dv$ is

$$\frac{\partial N}{\partial v} = \Lambda v^2 \exp\left(-\frac{mv^2}{2kT}\right) \tag{83}$$

or

$$\frac{\partial N}{\partial W} = \frac{2^{1/2}}{m^{3/2}} \Lambda W^{1/2} \exp\left(-\frac{W}{kT}\right) \tag{84}$$

where Λ is a constant and $W = mv^2/2$.

This is the so called **Maxwellian distribution**.

Clearly,

$$N = \int_0^\infty \frac{\partial N}{\partial v} dv = \Lambda \int_0^\infty v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv \tag{85}$$

where N (the total number of molecules) does not change with temperature.

It turns out that

$$\int_0^\infty v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv = \frac{\pi^{1/2}}{4} \left(\frac{2kT}{m}\right)^{3/2}. \tag{86}$$

Thus,

$$N = \Lambda \frac{\pi^{1/2}}{4} \left(\frac{2kT}{m}\right)^{3/2} \qquad \therefore \qquad \Lambda = 4N\pi^{-1/2} \exp\left(\frac{m}{2kT}\right)^{3/2}, \quad (87)$$

$$\frac{\partial N}{\partial v} = 4N\pi^{-1/2} \left(\frac{m}{2kT}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2kT}\right) \quad (88)$$

and

$$\frac{\partial N}{\partial W} = 2N\pi^{-1/2} \frac{W^{1/2}}{(kT)^{3/2}} \exp\left(-\frac{W}{kT}\right). \quad (89)$$

The shape of the $\partial N/\partial v$ versus v plot depends, of course, on the temperature, as shown in Figure 2.8, where T_0 is an arbitrary reference temperature. However, the area under the curve, being a measure of the total number of molecules in the gas, is independent of temperature.

The peak value of $\partial N/\partial v$ is

$$\frac{\partial N}{\partial v} = \frac{2N}{e} \left(\frac{2m}{\pi kT}\right)^{1/2}, \quad (90)$$

and occurs when $v = \sqrt{2kT/m}$ or, equivalently, when $W = kT$.

As T approaches 0, $\partial N/\partial v_{[max]}$ approaches ∞ and occurs for $v = 0$. The distribution becomes a delta function at $T = 0$.

This means that according to this classical theory, at absolute zero, all the molecules have zero velocity and zero energy.

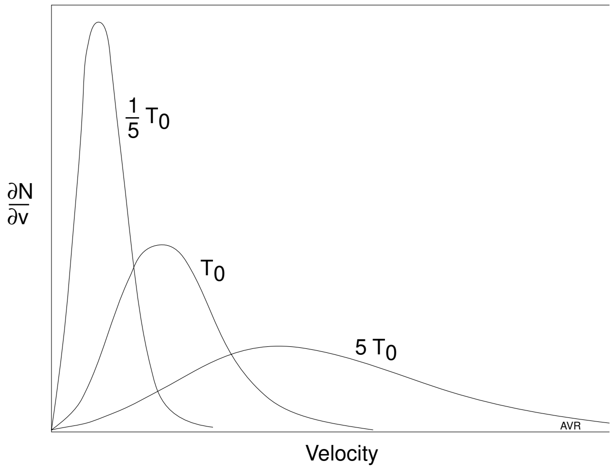

Figure 2.8 The Maxwellian velocity distribution at three different temperatures.

2.19 Fermi-Dirac Distribution

Electrons in metals do not behave in a Maxwellian way. They are governed by the **Pauli exclusion principle**, which states that in a given system, no two electrons can have the same quantum numbers, and, consequently, they cannot all have zero energy at absolute zero. Rather, at absolute zero electrons must be distributed uniformly in energy up to a given energy level. No electron has energy above this level, called the **Fermi level**. Thus, the probability, f, of finding electrons at a given energy level is:

$$f = 1, \quad \text{for } W < W_F \qquad \text{and} \quad f = 0 \quad \text{for } W > W_F. \tag{91}$$

As before, the number of allowed states with momenta less than $|p|$ (notice the change in terminology) is proportional to the volume of a sphere with radius $|p|$ in the momentum space:

$$N \text{ (with momenta less than } |p|) = \frac{2}{h^3}\left(\frac{4}{3}\pi p^3\right).$$

We have used $2/h^3$ as a proportionality constant. Although we will not present a justification for this, it should be noticed that the factor 2 is the result of 2 possible spins of the electron and that the dimensions come out right: N is the number of electrons per cubic meter.

Since $p = mv$, it follows that $p^2 = 2mW$ and

$$N \text{ (with momenta less than } |p|) = \frac{2}{h^3} \times \frac{4}{3}\pi (2mW)^{3/2}. \tag{92}$$

Thus

$$\frac{\partial N}{\partial W} = \frac{8\sqrt{2}\pi}{h^3} m^{3/2} W^{1/2}. \tag{93}$$

When the temperature is larger than zero, the probability that a given state be occupied is given by

$$f = \frac{1}{1 + \exp\left(\frac{W-\mu}{kT}\right)}. \tag{94}$$

The quantity μ is called the **chemical potential**. When $T = 0$, $\mu = W_F$ and the function above has the property that $f = 1$ for $W < W_F$ and $f = 0$ for $W > W_F$, as required. When $T \neq 0$, μ is slightly smaller than W_F.

The **density of states**, using this probability function becomes

$$\frac{\partial N}{\partial W} = \frac{8\sqrt{2}\pi}{h^3} m^{3/2} \frac{W^{1/2}}{1 + \exp\left(\frac{W-\mu}{kT}\right)} \tag{95}$$

and

$$N = \frac{8\sqrt{2}\pi}{h^3} m^{3/2} \int_0^\infty \frac{W^{1/2}}{1 + \exp\left(\frac{W-\mu}{kT}\right)} dW. \tag{96}$$

Since N is independent of T, the integral must itself be independent of T which means that the chemical potential, μ, must depend on T in just the correct manner.

For $kT \ll \mu$,

$$\int_0^\infty \frac{W^{1/2}}{1 + \exp\left(\frac{W-\mu}{kT}\right)} dW \approx \frac{2}{3}\mu^{3/2} = \frac{2}{3}W_F^{3/2}, \tag{97}$$

—that is, the integral does not depend on T and $\mu = W_F$.

At higher temperatures, to insure the invariance of the integral, μ must change with T approximately according to

$$\mu = W_F - \frac{(\pi kT)^2}{12 W_F}. \tag{98}$$

The difference between μ and W_F is small. For Fermi levels of 5 eV and T as high as 2000 K, it amounts to only some 0.1%. Therefore, for most applications, the chemical potential can be taken as equal to the Fermi level. One exception to this occurs in the study of the thermoelectric effect. Figure 2.9 shows a plot of the density of states, $\partial N/\partial W$, versus W for three temperatures. Notice that the chemical potential, which coincided with the Fermi level at $T = 0$, has shifted to a slightly lower energy at the higher temperature.

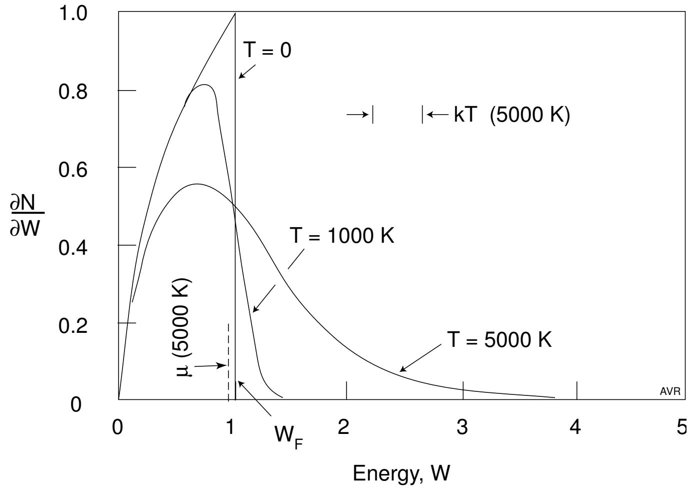

Figure 2.9 Energy distribution of electrons in a metal at three different temperatures.

2.20 Boltzmann's Law

A very useful result from statistical mechanics is **Boltzmann's law** that describes the concentration of particles in a gas as a function of their potential energy and their temperature. This law is used in a number of chapters in this book.

Consider a force, F, (derived from a potential) acting on each atom and aligned along the x-direction. nF is, of course, the total force acting on a cubic meter of gas and, if we restrict ourselves to a rectangular prism of base area, A, and height, dx, the force is $nFdxA$, and the pressure on the base is $nFdx$. In equilibrium, this pressure must balance the gas pressure, $kTdn$.

$$F dx = kT\frac{dn}{n}. \tag{99}$$

The potential energy, $W_{pot} = -\int F dx$, is

$$W_{pot} = -kT \ln n, \tag{100}$$

from which, we obtain Boltzmann's equation

$$n \propto \exp\left(-\frac{W_{pot}}{kT}\right). \tag{101}$$

Example

Atmospheric pressure

Each molecule in air has a potential energy, $mg\Delta h$ relative to a plane Δh meters closer to the ground.

According to Boltzmann's law, the concentration of molecules must vary as

$$n = n_0 \exp\left(-\frac{mg\Delta h}{kT}\right) \tag{102}$$

Note that kT/mg has the dimensions of length. It is called the **scale height**, H.

$$n = n_0 \exp\left(-\frac{\Delta h}{H}\right) \tag{103}$$

and, if T is independent of h,

$$p = p_0 \exp\left(-\frac{\Delta h}{H}\right). \tag{104}$$

(continued)

(continued)

In an isothermal atmosphere, the air pressure falls exponentially with height.

Taking the mean mass of the molecules in air as 29 daltons, and knowing that to convert daltons to kg, it suffices to divide by Avogadro's number, we find that the mass of a representative air molecule is about 48×10^{-27} kg. Consequently, the scale height of earth's atmosphere (isothermal at 300 K) is

$$H = \frac{1.38 \times 10^{-23} \times 300}{48 \times 10^{-27} \times 9.8} = 8,800 \quad \text{m.} \tag{105}$$

Appendix

Symbology

We will try to adopt the following convention for representing thermodynamic quantities such as

G, free energy,
H, enthalpy
Q, heat,
S, entropy, and
U, internal energy:

1. Capital letters will indicate the quantity associated with an arbitrary amount of matter or energy.
2. Lower case letter indicate the quantity per unit. A subscript may be used to indicate the species being considered. For example, the free energy per kilomole of H_2 will be represented by $\overline{g_{H_2}}$.

g = free energy per kilogram.
$\overline{g}$ = free energy per kilomole.
g^* = free energy per kilogram, at 1 atmosphere pressure.
$\overline{g}^*$ = free energy per kilomole, at 1 atmosphere pressure.
$\overline{g}_f$ = free energy of formation per kilomole.
$\overline{g}_f^\circ$ = free energy of formation per kilomole, at 298 K, 1 atmosphere, i.e., at RTP, (Standard Free Energy of Formation).

For more information on some topics in this chapter, read:

Çengel, Y. A., and M. A. Boles, *Thermodynamics, an engineering approach*, McGraw-Hill, **1994**.

PROBLEMS

2.1 10 kg/s of steam ($\gamma = 1.29$) at 2 MPa are delivered to an adiabatic turbine (100% efficient). The exhaust steam is at 0.2 MPa and 400 K.

1. What is the intake temperature?
2. What power does the turbine deliver?

2.2 Show that the cylinder and piston experiment of Section 3.14 (with the solid object inside) is reversible provided the compression is carried out infinitely slowly. Do this numerically. Write a computer program in which compression and expansion take place in suitably small steps and are, in each step, followed by an equalization of temperature between the gas and the solid object within the cylinder.

2.3 Refer to the experiment described in Section 3.10. Show that the work done in lifting the 1 kg mass in two steps (first 2 kg, then 1 kg) is 14.2 J. Show that the 2 kg mass rises 0.444 m. Assume that the steps occur slowly enough so that the gas cooled by the expansion, returns to the original temperature after each step.

2.4 Consider 10 m^3 (V_0) of gas ($\gamma = 1.6$) at 10^5 Pa (p_0) and 300 K (T_0).

1. How many kilomoles, μ, of gas are involved?
2. The gas is compressed isothermally to a pressure, p_f, of 1 MPa.
   - 2.1 What is the new volume, V_f?
   - 2.2 How much energy was used in the compression?
3. Now, instead of compressing the gas isothermally, start again (from V_0, p_0, and T_0) and compress the gas adiabatically to a pressure, p_2. The gas will heat up to T_2. Next, let it cool down isometrically (i.e., without changing the volume) to $T_3 = 300$ K and a pressure, p_3, of 1 MPa. In other words, let the state return to that after the isothermal compression.
   - 3.1 What is the pressure, p_2?
   - 3.2 What is the temperature, T_2, after the adiabatic compression?
   - 3.3 What is the work done during the adiabatic compression?
   - 3.4 Subtract the heat rejected during the isometric cooling from the work done during the adiabatic compression to obtain the net energy change owing to the process described in Item c.

2.5 When a gas expands, it does an amount of work

$$W = \int_{V_0}^{V_1} p dV.$$

If the expansion is adiabatic, the polytropic law is observed and the integral becomes (see Chapter 6)

$$W = \frac{p_0 V_0^\gamma}{\gamma - 1}\left(V_1^{1-\gamma} - V_0^{1-\gamma}\right).$$

Show, by using the definitions of c_v and of γ, that this work is equal to the energy needed to raise the temperature of the gas from T_0 to T_1 under constant volume conditions.

2.6 The domains in a nonmagnetized ferromagnetic material are randomly oriented, however, when magnetized, these domains are reasonably well aligned. This means, of course, that the magnetized state has a lower total entropy than the nonmagnetized state.

There are materials (gadolinium, Gd, for example) in which this effect is large. At 290 K, polycrystalline gadolinium (atomic mass 157.25, density 7900 kg/m^3) has a total entropy of 67.6 kJ K^{-1} kmole^{-1} when unmagnetized and 65.6 kJ K^{-1} kmole^{-1} when in a 7.5 tesla field.

Assume that 10 kg of Gd are inside an adiabatic container, in a vacuum, at a temperature of 290 K. For simplicity, assume that the heat capacity of the container is negligible. The heat capacity of Gd, at 290 K, is 38.4 kJ K^{-1} kmole^{-1}.

Estimate the temperature of the gadolinium after a 7.5 T field is applied.

2.7 The French engineer, Guy Negre, invented an "eco-taxi," a low pollution vehicle to be built in Mexico beginning in the year 2001. Its energy storage system consist of compressed air tanks that, on demand, operate an engine (it could be a turbine, but in the case of this car, it is a piston device).

There are several problems to be considered. Let us limit ourselves to the turn around efficiency of the energy storage system. For comparison, consider that a led-acid battery has a turn around efficiency of somewhat over 70% and fly wheels, more than 90%.

A very modern compressed gas canister can operate at 500 atmospheres.

1. Calculate the energy necessary to compress 1 kilomole of air ($\gamma = 1.4$) *isothermally* from 1 to 500 atmospheres. The temperature is 300 K.
2. One could achieve the same result by compressing the air adiabatically and then allowing it to cool back to 300 K. Calculate the energy necessary to accomplish this.
3. The compressed air (at 300 K) is used to drive a turbine (in the French scheme, a piston engine). Assume that the turbine is ideal—**isentropic**—and it delivers an amount of mechanical energy equal to the change of enthalpy the gas undergoes when expanding. How much

energy does 1 kilomole of air deliver when expanding under such conditions?

To solve this problem, follow the steps suggested below.

3.1. Write an equation for the change of enthalpy across the turbine as a function of the input temperature (300 K) and the unknown output temperature.

3.2. Using the polytropic law, find the output temperature as a function of the pressure ratio across the turbine. Assume that the output pressure is 1 atmosphere.

If you do this correctly, you will find that the temperature at the exhaust of the turbine is below the liquefaction point of the gases that make up air. This would interfere with the turbine operation, but in the present problem, disregard this fact.

3.3.Once you have the exhaust temperature, calculate the mechanical energy generated by the turbine.

4. What is the turn around efficiency of the compressed air energy storage system under the (optimistic) assumptions of this problem—that is, what is the ratio of the recovered energy to the one required to compress the air?

2.8 The cylinder in the picture has, initially, a 1 liter volume and is filled with a given gas at 300 K and 10^5 Pa. It is perfectly heat insulatless piston has no mass and piston and cylinder, as well as the 1-ohm electric resistor, installed inside the device have negligible heat capacity.

At the beginning of the experiment, the piston is held in place, so it cannot move.

A 10-amp dc current is applied for 1 second. causing the pressure to rise to 1.5×10^5 pascals. Next, the piston is released and rises.

What is the work done by the piston?

2.36