

## CHAPTER FOUR

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# The first law of thermodynamics

### 4.1 Work

As we have already mentioned, in atmospheric thermodynamics we will be dealing with equilibrium states of air. If a system (parcel of air, for example) is at equilibrium with its environment no changes take place in either of them. We can imagine the “shape” of the parcel remaining unchanged in time. If the pressure of the surroundings changes, then the force associated with the pressure change will disturb the parcel thereby forcing it away from equilibrium. In order for the parcel to adjust to the pressure changes of the surroundings, the parcel will either contract or expand. If the parcel expands we say that the parcel performs work on the environment and if the parcel contracts we say that the environment performs work on the parcel. By definition, if the volume change is  $dV$  then the incremental work done,  $dW$ , is

$$dW = pdV.$$

Accordingly, when the system changes from an initial state  $i$  to a final state  $f$  the total work done, either by the system or on the system, is

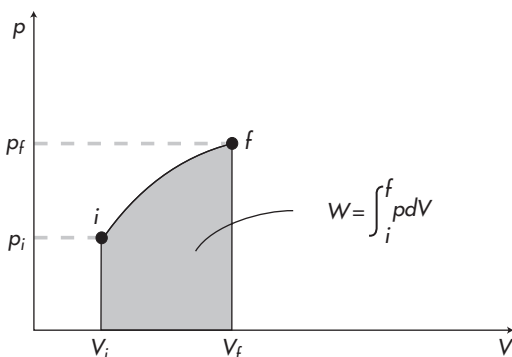
$$W = \int_i^f pdV.$$

The above equation indicates that the work done is given by an area in a  $(p, V)$  diagram (Figure 4.1) [or a  $(p, a)$  diagram, where  $a$  is the specific volume]. If  $dV > 0$  (the system expands) it follows that  $W > 0$  and if  $dV < 0$  (system contracts) it follows that  $W < 0$ . Thus, positive work corresponds to work done by the system on the environment and negative work corresponds to work done to the system by the environment.

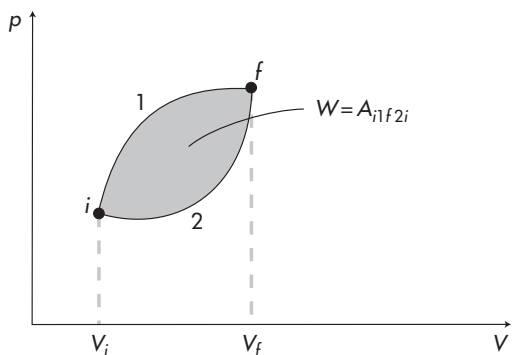
Now let us consider a situation where the system expands through a reversible transformation from  $i$  to  $f$  and then contracts

**Figure 4.1**

The shaded area gives the work done when a system changes from an initial state  $i$  to a final state  $f$ .

**Figure 4.2**

The shaded area gives the work done during a cyclic reversible transformation.



from  $f$  to  $i$  along exactly the same path in the  $(p, V)$  diagram. Then, the total work done will be

$$W = \int_i^f p dV + \int_f^i p dV = \int_i^f p dV - \int_i^f p dV = 0.$$

If, however, the system expands from  $i$  to  $f$  and then contracts from  $f$  to  $i$  but along a different reversible transformation (different path), then the total work done would be (see Figure 4.2)

$$\begin{aligned} W &= \left[ \int_i^f p dV \right]_1 + \left[ \int_f^i p dV \right]_2 \\ &= \text{area under curve 1} - \text{area under curve 2} \\ &= A_{i1f2i} \neq 0 \end{aligned}$$

where  $A_{i1f2i}$  is the area enclosed by the two paths. It follows that  $\oint dW = \oint p dV \neq 0$  and thus  $dW$  is not an exact differential, which means that work is not a state function. As such it depends on the particular way the system goes from  $i$  to  $f$ . Because of this from now on we will denote the incremental change in work as  $\delta W$  not as  $dW$ .

If we write  $dV = dA ds$  (where  $dA$  is an area element and  $ds$  a distance element) we have that  $\delta W = p dA ds = F ds = F v dt$  or that

$$\frac{\delta W}{dt} = Fv$$

or

$$\frac{\delta W}{dt} = m \frac{dv}{dt} v$$

or

$$\frac{\delta W}{dt} = \frac{d}{dt} \left( \frac{1}{2} m v^2 \right)$$

or

$$\frac{\delta W}{dt} = \frac{dK}{dt} \quad (4.1)$$

where  $v$  denotes the velocity of the parcel and  $K$  is the kinetic energy of the parcel. It follows that the work done and the kinetic energy are related. The last equation indicates that one way by which a thermodynamic system can exchange energy with its environment is by performing work. The other is through transfer of heat. More on that will follow soon. According to (4.1) the units for work are those of energy. Thus, the unit for work in the MKS system is the joule which is defined as  $J = N m$  where the newton  $N = kg m s^{-2}$ . In the cgs system, the unit is the erg which is defined as  $erg = dyn cm$  where  $dyn = g cm s^{-2}$ . It follows that  $1 \text{ joule} = 10^7 \text{ erg}$ .

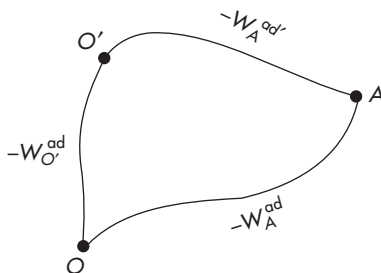
## 4.2 Definition of energy

The first law of thermodynamics expresses the principle of conservation of energy for thermodynamical systems. The idea here is that energy cannot be created or destroyed. It can only change from one form to another. In this regard if during a transformation the energy of the system increases by some amount, then this amount is equal to the amount of energy the system receives from its surroundings in some other form.

Let us consider a closed system contained in an *adiabatic* enclosure. In this case the energy of the system,  $U$ , is equal to the sum of the potential and kinetic energy of all its molecules. The sum of the energies of all molecules depends on the state of the system at a given moment (i.e. on the values  $p, V, T$ ) but obviously is independent of past states. It follows that the internal energy of the system depends on the state in which it exists but not on the way it arrived at that state. Thus, in a transformation  $i \rightarrow f$ ,  $\Delta U = U_f - U_i$ . Then, for a cyclic transformation,  $\oint \Delta U = 0$  which means that for an infinitesimal process  $dU$  is an exact differential. If no external forces are acting upon the system (i.e. the system is at equilibrium

**Figure 4.3**

The work done by an external force on a system that is taken adiabatically from a reference state  $O$  or a reference state  $O'$  to a state  $A$ . In this case the work done depends on the initial and final states, not on the particular path from an initial state to a final state.



with its environment), then its energy remains the same ( $\Delta U = 0$ ). If some external force acts upon the system taking it from state  $i$  to state  $f$  then the conservation of energy principle dictates that

$$U_f - U_i = -W^{\text{ad}} \quad (4.2)$$

where  $-W^{\text{ad}}$  is the work done adiabatically by the external force on the system ( $+W^{\text{ad}}$  is the work done by the system). Note that equation (4.2) implies that the work done in this case depends only on states  $i$  and  $f$ , *not* on the particular transformation  $i \rightarrow f$ . This is contrary to what we proved previously – that the work done is *not* an exact differential and that it depends on the particular transformation  $i \rightarrow f$ . The discrepancy is due to the fact that here we are dealing with adiabatic transformations. Only in this case does the work done not depend on the particular transformation.

Assume now a standard state  $O$  of this system where by definition  $U_O = 0$  and a state  $A$  where  $U_A \neq 0$ . Assume further that through some external influences we take the system from state  $O$  to state  $A$ . Then according to equation (4.2) the energy of state  $A$  is

$$U_A = -W_A^{\text{ad}}. \quad (4.3)$$

Apparently, equation (4.3) (and hence any definition of energy) depends on the standard state  $O$ . If instead of  $O$  we had chosen another standard state  $O'$  we would have obtained  $U'_A$ . In this case (see Figure 4.3) we would have (since  $W^{\text{ad}}$  depends on initial and final states only)

$$-W_A^{\text{ad}} = -W_A^{\text{ad}'} - W_{O'}^{\text{ad}}$$

or

$$U_A = U'_A + U_{O'}$$

or

$$U_A - U'_A = U_{O'}$$

where  $U_{O'}$  is the energy of the standard state  $O'$  and thus is a constant. It follows that had we chosen a different standard state,  $U'_A$  would differ by a constant (additive) amount. This constant is an essential feature of the concept of energy which has no effect on

the final results when we are working with differences (changes) of energy and not with actual amounts.

### 4.3 Equivalence between heat and work done

Consider a sample of water at a state  $i$  where the temperature is  $T_i$  and at a state  $f$  where the temperature is  $T_f > T_i$ . In how many different ways can we take the system from  $i$  to  $f$ ? Obviously we can simply warm up the system. In this case, and as long as  $T_f$  is low enough for evaporation to be negligible, the volume of the system remains unchanged and therefore no work is done by the external forces. This is the first way. The second way is to raise the temperature via friction. Just imagine a set of paddles rotating inside the system. In this case, we will observe that as long as the paddles continue to rotate the temperature of the water increases. Since the water resists the motion of the paddles we must perform mechanical work in order to keep the paddles moving until  $T_f$  is reached.

Thus, the work performed by the system depends on whether we go from  $i$  to  $f$  by means of the first or the second way. If we assume that the principle of the conservation of energy holds, then we must admit that the energy transmitted to the water in the form of mechanical work from the rotating paddles is transmitted to the water in the first way in a non-mechanical form called *heat*. It follows that heat and (mechanical) work are equivalent and two different aspects of the same thing: energy. In the first way, where no work is performed, the change of energy can be expressed as

$$\Delta U = Q_{W=0}$$

where  $Q_{W=0}$  is the amount of heat received. In the second way (the experiment can be thought of as taking place in some adiabatic enclosure) the change in energy can be expressed as

$$\Delta U = -W^{\text{ad}}.$$

When both work and heat are allowed to be exchanged, we replace the above equations by the general expression

$$\Delta U + W = Q. \quad (4.4)$$

The quantity  $Q_{W=0}$  required to raise 1 g of water from 14.5 °C to 15.5 °C is by definition equal to 1 cal. In this case  $W^{\text{ad}}$  turns out to be equal to 4.185 J. This value is known as the mechanical equivalent of heat. Note that since  $\delta W$  is not an exact differential,  $\delta Q$  is not either. Thus, for an infinitesimal process the above equation takes the form

$$dU + \delta W = \delta Q. \quad (4.5)$$

Note that for a cyclic transformation  $\oint dU = 0$  and thus  $W = Q$ . Equation (4.5) is the mathematical expression of the first law of thermodynamics. Since  $\delta W = pdV$  we can write the first law as:

$$dU + pdV = \delta Q \quad (4.6)$$

or for unit mass

$$du + pda = \delta q. \quad (4.7)$$

#### 4.4 Thermal capacities

Since  $dU$  is an exact differential we can write it as:

$$dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \quad (4.8)$$

or as:

$$dU = \left( \frac{\partial U}{\partial T} \right)_p dT + \left( \frac{\partial U}{\partial p} \right)_T dp \quad (4.9)$$

or as:

$$dU = \left( \frac{\partial U}{\partial p} \right)_V dp + \left( \frac{\partial U}{\partial V} \right)_p dV. \quad (4.10)$$

By combining equations (4.6) and (4.8) we get

$$\left( \frac{\partial U}{\partial T} \right)_V dT + \left[ p + \left( \frac{\partial U}{\partial V} \right)_T \right] dV = \delta Q \quad (4.11)$$

By combining equations (4.6) and (4.9) and using the fact that

$$dV = \left( \frac{\partial V}{\partial p} \right)_T dp + \left( \frac{\partial V}{\partial T} \right)_p dT$$

we arrive at

$$\left[ \left( \frac{\partial U}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p \right] dT + \left[ \left( \frac{\partial U}{\partial p} \right)_T + p \left( \frac{\partial V}{\partial p} \right)_T \right] dp = \delta Q. \quad (4.12)$$

By combining (4.6) and (4.10) we get

$$\left( \frac{\partial U}{\partial p} \right)_V dp + \left[ \left( \frac{\partial U}{\partial V} \right)_p + p \right] dV = \delta Q. \quad (4.13)$$

We define as thermal capacity,  $C$ , the ratio  $\delta Q/dT$  and we denote it as  $C_V$  if the thermal capacity is measured at a constant  $V$  and as  $C_p$  if it is measured at constant  $p$ . According to this definition if in a process at constant volume there is no change of the physical and

chemical state of a homogeneous system, then the heat absorbed is proportional to the variation in temperature

$$\delta Q = C_V dT$$

or

$$\delta Q = c_V m dT$$

where  $m$  is the mass of the system and  $c_V$  is the specific heat capacity at constant volume (i.e.  $c_V = C_V/m$ ). Another specific heat is the molar specific heat  $c_{Vm} = C_V/n$  where  $n$  is the number of moles. Similarly, at constant pressure

$$\delta Q = C_p dT$$

or

$$\delta Q = c_p m dT.$$

From equation (4.11) if we set  $dV = 0$  we obtain

$$C_V = \frac{\delta Q}{dT} = \left( \frac{\partial U}{\partial T} \right)_V$$

(4.14)

and

$$c_V = \left( \frac{\partial u}{\partial T} \right)_a.$$

From equation (4.12) if we set  $dp = 0$  we obtain

$$C_p = \left( \frac{\partial U}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p.$$

By defining here a new state function, the enthalpy,  $H = U + pV$  ( $h = u + pa$ ), it follows from the above equation that

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p$$

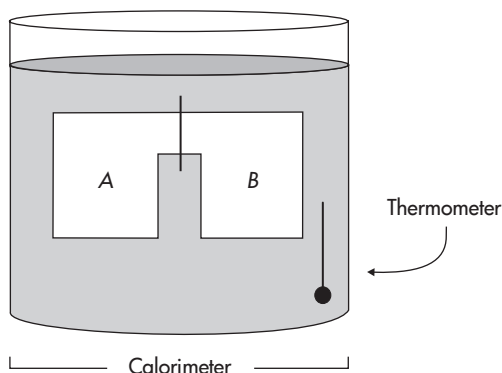
(4.15)

and

$$c_p = \left( \frac{\partial h}{\partial T} \right)_p.$$

Again here we can define the molar specific heat at constant pressure as  $c_{pm} = C_p/n$ . Also, since  $pV = nR^*T$ , for ideal gases the enthalpy is a function of two state variables ( $U, T$ ) and as such it can be expressed as an exact differential. Note that for isobaric processes  $dH = dU + pdV = \delta Q$ , i.e. the change in enthalpy equals the amount of heat absorbed or given away.

**Figure 4.4**  
The experimental design  
of Joule's proof that  
 $U = U(T)$ .



#### 4.5 More on the relation between $U$ and $T$ (Joule's law)

As we have stated earlier, any thermodynamical quantity can be expressed as a function of two state variables. As such we can assume that  $U = f(V, T)$ . In Chapter 2 we discussed the fact that the kinetic theory of heat accepts that  $U$  is proportional to the absolute temperature. This indicates that  $U$  is a function of only one state variable,  $U = f(T)$ . An experimental proof of this was provided by Joule, who performed the following experiment. He constructed a calorimeter and placed in it a container having two chambers,  $A$  and  $B$ , separated from each other by a stopcock (see Figure 4.4). He filled  $A$  with an ideal gas and evacuated  $B$ . After the whole system settled to a thermal equilibrium (as indicated by the thermometer in the calorimeter), Joule opened the stopcock thus allowing the ideal gas to flow from  $A$  to  $B$  until pressure everywhere equalized. He observed that this did not cause any change in the temperature reading. From the first law we thus have  $Q = 0$  or from equation (4.4)

$$\Delta U = -W.$$

Now note that since the volume of the system (the container) does not change, the system performs no work. As such  $W = 0$  and  $\Delta U = 0$ . But, you may ask, how about the gas inside chamber  $A$ ? Its volume increases as it expands to fill container  $B$ . What is the effect of that? Since there was no temperature change and no variation in energy during the process we must conclude that a variation in volume at a *constant temperature* produces no variation in energy. In other words  $U \neq f(V)$  which means that  $U$  is only a function of  $T$ :

$$U = U(T). \quad (4.16)$$

Later in problem 6.2 you will be asked to prove this mathematically.



**More on thermal capacities**

Because of equation (4.16),  $(\partial U/\partial T)_V = dU/dT$ . As such we can write equation (4.14) as

$$C_V = \frac{dU}{dT} \quad (4.17)$$

$$c_V = \frac{du}{dT}.$$

Similarly,  $H = U + pV = U + nR^*T = H(T)$  and

$$C_p = \frac{dH}{dT} \quad (4.18)$$

$$c_p = \frac{dh}{dT}.$$

In the atmospheric range of temperatures,  $c_V$  and  $c_p$  are nearly constant. From equation (4.17) we then have that

$$U = \int C_V dT + \text{constant}$$

or

$$U = C_V T + \text{constant}.$$

Since only differences in internal energy (and thus in enthalpy) are physically relevant, we can set the integration constant to zero and obtain

$$U \approx C_V T.$$

Similarly  $H \approx C_p T$ ,  $u \approx c_V T$ , and  $h \approx c_p T$ . Equations (4.17) and (4.18) can be combined to obtain

$$C_p - C_V = nR^* \quad (4.19)$$

which implies that

$$c_p - c_V = R, \quad c_{pm} - c_{Vm} = R^*. \quad (4.20)$$

Recall now from Chapter 2 (equation (2.8)) that for a *monatomic* gas consisting of  $N$  point-masses the total internal energy is

$$U = \frac{3}{2} NkT.$$

It follows that

$$C_V = \frac{dU}{dT} = \frac{3}{2} Nk = \frac{3}{2} mR = \frac{3}{2} nMR = \frac{3}{2} nR^*,$$

and

$$c_{Vm} = \frac{3}{2}R^*, \quad c_V = \frac{3}{2} \frac{n}{m} R^* = \frac{3}{2}R.$$

Similarly,

$$C_p = \frac{dH}{dT} = \frac{dU}{dT} + nR^* = \frac{5}{2}nR^*,$$

and

$$c_{pm} = \frac{5}{2}R^*, \quad c_p = \frac{5}{2}R.$$

For a diatomic gas these values change to

$$C_V = \frac{5}{2}nR^*, \quad c_{Vm} = \frac{5}{2}R^*, \quad c_V = \frac{5}{2}R$$

and

$$C_p = \frac{7}{2}nR^*, \quad c_{pm} = \frac{7}{2}R^*, \quad c_p = \frac{7}{2}R.$$

Note that often in the literature the values of  $C_V$  and  $c_{Vm}$  or  $C_p$  and  $c_{pm}$  are assumed the same. This is correct only in the case of *one mole*. From the above it follows that

$$\frac{C_p}{C_V} = \frac{c_{pm}}{c_{Vm}} = \frac{c_p}{c_V}.$$

We will denote these ratios as  $\gamma$ .

Dry air is considered a diatomic gas. According to the above relationships we estimate that for dry air

$$\begin{aligned} \gamma_d &= 1.4 \\ c_{Vd} &= 718 \text{ J kg}^{-1} \text{ K}^{-1} = 171 \text{ cal kg}^{-1} \text{ K}^{-1} \\ c_{pd} &= 1005 \text{ J kg}^{-1} \text{ K}^{-1} = 240 \text{ cal kg}^{-1} \text{ K}^{-1} \\ R_d &= 287 \text{ J kg}^{-1} \text{ K}^{-1}. \end{aligned}$$

According to the above definitions we can write the first law as:

$$C_V dT + p dV = \delta Q \quad (4.21)$$

or

$$c_V dT + p da = \delta q$$

Considering that  $C_V = C_p - nR^*$  and that  $pV = nR^*T$ , equation (4.21) becomes

$$(C_p - nR^*)dT + (nR^*dT - Vdp) = \delta Q$$

or

$$C_p dT - V dp = \delta Q. \quad (4.22)$$

For convenience Table 4.1 summarizes all the different expressions of the first law.

Table 4.1. *Expressions of the first law*

For a gas of mass $m$	For unit mass
$dU + \delta W = \delta Q$	$du + \delta w = \delta q$
$dU + pdV = \delta Q$	$du + pda = \delta q$
$C_V dT + pdV = \delta Q$	$c_V dT + pda = \delta q$
$C_p dT - Vdp = \delta Q$	$c_p dT - adp = \delta q$

## 4.6 Consequences of the first law

Let us look at the form of the first law in the following special cases.

• **Isothermal transformations:**  $i \xrightarrow{T=\text{constant}} f$

During such transformations  $dT = 0$  and as such from equation (4.21) it follows that  $\delta Q = \delta W$ . Then the amount of heat exchanged is

$$Q = \int_i^f \delta W = \int_i^f p dV$$

or

$$Q = nR^*T \int_i^f \frac{dV}{V}$$

or

$$Q = nR^*T \ln \frac{V_f}{V_i}.$$

• **Isochoric transformations:**  $i \xrightarrow{V=\text{constant}} f$

In this case  $dV = 0$  and from the first law it follows that

$$\delta Q = dU = C_V dT$$

or

$$\Delta U = Q = C_V \int_i^f dT = C_V (T_f - T_i).$$

• **Isobaric transformations:**  $i \xrightarrow{p=\text{constant}} f$

In this case it follows that

$$\delta Q = C_p dT \quad \text{or} \quad Q = C_p (T_f - T_i),$$

$$\delta W = p dV \quad \text{or} \quad W = p(V_f - V_i).$$

and

$$\Delta U = C_p(T_f - T_i) - p(V_f - V_i)$$

• **Cyclic transformations**  $i \longrightarrow f \longrightarrow i$

As we know, in cyclic transformations  $\oint dU = 0$ . Then, from the first law it follows that

$$\oint \delta W = \oint \delta Q.$$

• **Adiabatic transformations – Poisson's relations**

During an adiabatic process there is no exchange of heat between a system and its surroundings by virtue of temperature differences between them. Thus,  $\delta Q = 0$ . Then the first law can be expressed as

$$dU = -\delta W$$

or

$$C_V dT = -pdV$$

or

$$C_p dT = V dp$$

or

$$\frac{dT}{T} = \frac{V}{C_p} \frac{dp}{T}$$

or using  $pV = mRT$

$$\frac{dT}{T} = \frac{mR}{C_p} \frac{dp}{p}$$

or

$$\frac{dT}{T} = \frac{nR^*}{C_p} \frac{dp}{p}$$

or using  $C_p - C_V = nR^*$

$$\frac{dT}{T} = \left(1 - \frac{C_V}{C_p}\right) \frac{dp}{p}$$

or

$$\frac{dT}{T} = \left(1 - \frac{1}{\gamma}\right) \frac{dp}{p}. \quad (4.23)$$

Integrating equation (4.23) yields

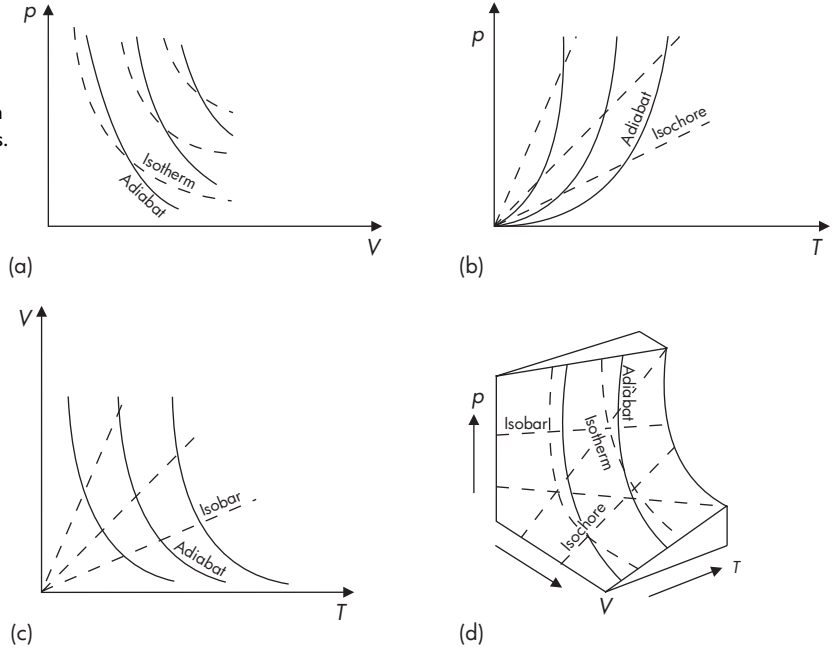
$$\ln T = \left(1 - \frac{1}{\gamma}\right) \ln p + \ln(\text{constant})$$

or

$$\ln T = \ln p^{\frac{\gamma-1}{\gamma}} + \ln(\text{constant})$$

**Figure 4.5**

The various relationships between adiabats, isotherms, isobars, and isochores in partial and in the complete state spaces.



or

$$T = \text{constant} \times p^{\frac{\gamma-1}{\gamma}}$$

or

$$Tp^{\frac{1-\gamma}{\gamma}} = \text{constant}. \quad (4.24)$$

Through the ideal gas law we can then derive the following equivalent expressions of equation (4.24):

$$TV^{\gamma-1} = \text{constant} \quad (4.25)$$

$$pV^{\gamma} = \text{constant}. \quad (4.26)$$

Equations (4.24)–(4.26) express Poisson's relations for adiabatic processes. Since for dry air  $\gamma = 1.4 > 0$  equation (4.25) proves something that we all more or less know: that as an air parcel rises and expands (i.e.  $V$  increases), its temperature must decrease. For adiabatic expansion, since  $\delta Q$  is zero this decrease is due to expansion work that the parcel performs on the environment.

From the ideal gas law it follows that isotherms are given by the equation

$$pV = \text{constant}.$$

Thus on a  $(p, V)$  diagram isotherms are equilateral hyperbolas (Figure 4.5(a); an equilateral hyperbola is one whose asymptotes are perpendicular to each other). From equation (4.26) we see that the adiabats on a  $(p, V)$  diagram will also be equilateral hyperbolas but since  $\gamma > 1$  the adiabats will be steeper than the

isotherms. Obviously in a  $(p, V)$  diagram isobaric and isochoric transformations are represented by straight lines on the  $p$  and  $V$  axis, respectively. On a  $(p, T)$  diagram the isochores are given by the equation

$$V = \frac{nR^*T}{p} = \text{constant}'$$

or

$$Tp^{-1} = \text{constant}$$

which is the equation of a straight line. From equation (4.24) it also follows that in a  $(p, T)$  diagram the adiabats are again hyperbolas (Figure 4.5(b)). On a  $(T, V)$  diagram (Figure 4.5(c)) the isobars are straight lines (as before  $TV^{-1} = \text{constant}$ ) and the adiabats are hyperbolas (see equation (4.25)). The complete  $(p, V, T)$  space and transformations are shown in Figure 4.5(d). Since they require no heat exchange between a parcel and its environment (i.e. they require perfect isolation), adiabatic processes are idealizations that never happen in nature. However, for processes that happen quickly, energy transfer is not very significant. Such processes are thus adiabatic to a good approximation.

#### • Polytropic transformations

During an isothermal transformation the system can exchange heat with its environment but its temperature remains constant. This, however, is an ideal situation. In reality the equilization of temperatures does not happen instantaneously. Similarly, an adiabatic transformation is an ideal situation since it requires perfect heat insulation. The same comments can be made for isobaric and isochoric transformations. Thus, the relations  $pV = \text{constant}$ ,  $pV^\gamma = \text{constant}$ ,  $Tp^{-1} = \text{constant}$ , and  $TV^{-1} = \text{constant}$  are special cases of the general relationship  $pV^\eta = \text{constant}$  where  $\eta$  can take on any value. Such transformations are called *polytropic transformations* (in Greek polytropic means multi-behavioral). If we assume that  $\eta = \gamma/\epsilon$  where  $\epsilon$  is a constant, we can work our way backwards from equation  $pV^\eta = \text{constant}$  or  $Tp^{\frac{1-\eta}{\eta}} = \text{constant}$  to arrive at

$$\frac{dT}{T} = \left(1 - \frac{\epsilon}{\gamma}\right) \frac{dp}{p}.$$

Considering that  $\gamma = \frac{C_p}{C_v}$  the above equation can be expressed as

$$\frac{dT}{T} = \left(\frac{C_p - C_v\epsilon}{C_p}\right) \frac{dp}{p}$$

or

$$\frac{dT}{T} = \left(\frac{C_p - C_v - C_v\epsilon + C_v}{C_p}\right) \frac{dp}{p}$$

or

$$\frac{dT}{T} = \left( \frac{C_p - C_v}{C_p} \right) \frac{dp}{p} + \frac{C_v(1 - \epsilon)}{C_p} \frac{dp}{p}$$

or

$$\frac{dT}{T} = \frac{nR^*}{C_p} \frac{dp}{p} + \frac{(1 - \epsilon)}{\gamma} \frac{dp}{p}$$

or

$$\frac{dT}{T} = \frac{V}{C_p} \frac{dp}{T} + \frac{(1 - \epsilon)}{\gamma} \frac{dp}{p}$$

or

$$C_p dT = V dp + \frac{(1 - \epsilon) C_p T}{\gamma p} dp$$

or

$$C_p dT = V dp - \frac{C_p(\epsilon - 1)}{\gamma} \frac{V}{nR^*} dp.$$

Then, according to the first law, the second term on the right-hand side is the heat exchanged, which is zero if  $\epsilon = 1$  (i.e.  $\eta = \gamma$ , adiabatic process), greater than zero (i.e. the system absorbs heat from the environment) if  $\eta < \gamma$  ( $\epsilon > 1$ ) and  $dp < 0$ , or  $\eta > \gamma$  ( $\epsilon < 1$ ) and  $dp > 0$ , and less than zero (i.e. the system gives away heat to the environment) if  $\eta > \gamma$  and  $dp < 0$ , or  $\eta < \gamma$  and  $dp > 0$ . From the above equation we also find that for  $\epsilon = 0$  (i.e.  $\eta = \infty$ )  $nR^* dT = V dp$ , which owing to the ideal gas law implies  $dV = 0$ . For  $\epsilon = \gamma$  (i.e.  $\eta = 1$ ), it reduces to  $C_p dT = 0$ , while for  $\epsilon = \infty$  (i.e.  $\eta = 0$ ) it dictates that  $dp = 0$ . As such a polytropic process  $pV^\eta = \text{constant}$  reduces to an isobaric, to an isothermal, to an adiabatic, and to isochoric process for  $\eta = 0, 1, \gamma$ , and  $\infty$ , respectively.

Having said this we must add that in the atmosphere over a rather wide range of motions the timescale for an air parcel (our system) needed to adjust to environmental changes of pressure, and to perform work, is short compared with the corresponding timescale of heat transfer. For example, above the boundary layer and outside the clouds the timescale of heat transfer is about two weeks whereas the timescale of displacements that affect a parcel is of the order of hours to a day. It thus appears that adiabatic approximations are good approximations for many atmospheric phenomena.

#### • Dry adiabatic lapse rate

From equation (4.24) we have

$$T = \text{constant} \cdot p^{\frac{\gamma-1}{\gamma}}.$$

By taking the logarithmic derivative of the above equation we have

$$d \ln T = \frac{\gamma-1}{\gamma} d \ln p$$

or

$$\frac{dT}{T} = \frac{\gamma - 1}{\gamma} \frac{dp}{p}$$

or

$$\frac{1}{T} \frac{dT}{dz} = \frac{\gamma - 1}{\gamma} \frac{1}{p} \frac{dp}{dz}. \quad (4.27)$$

For large-scale motions the hydrostatic approximation states that pressure gradient force balances the force due to gravity. Therefore,

$$\frac{dp}{dz} = -\rho g. \quad (4.28)$$

For a parcel of air rising in the atmosphere, equation (4.27) is valid as long as its ascent is an adiabatic process. For the same parcel equation (4.28) is valid only if  $dp/dz$  experienced by the parcel is equal to that of the large scale (surroundings). We assume this is more or less true but in equation (4.28)  $\rho$  represents the density of the surroundings which from the ideal gas law is

$$\rho = \frac{p}{RT_s} \quad (4.29)$$

where  $T_s$  denotes the temperature of the surroundings. In this case by combining equations (4.27)–(4.29) we have that

$$\frac{dT}{dz} = -\frac{\gamma - 1}{\gamma} \frac{g}{R} \frac{T}{T_s}.$$

Recall that by definition an adiabatic ascent or descent is one in which there is no exchange of energy with its surroundings by virtue of temperature differences between them. Accordingly, if the parcel remains dry (i.e. no condensation takes place) we may define from the above equation the dry adiabatic lapse rate,  $\Gamma_d$ , as the atmospheric temperature profile such that the temperature of the parcel is always at the temperature of its surroundings. For such a profile  $T = T_s$  and as such for dry air

$$\Gamma_d = -\frac{dT}{dz} = \frac{\gamma - 1}{\gamma} \frac{g}{R_d} = \frac{g}{c_{pd}} = 9.8^\circ\text{C km}^{-1}. \quad (4.30)$$

This value is larger than the observed average decrease of environmental temperature with altitude. The difference is mainly due to the fact that in the derivation of  $\Gamma_d$  we neglected the presence of water vapor. When vapor is present we have new lapse rates, which we will discuss in a later chapter.

Recalling that  $h = u + pa$  and that  $h = c_{pd}T$  we can write equation (4.30) as

$$\frac{dh}{dz} = -g$$



or

$$\frac{d}{dz}(h + gz) = 0 \quad (4.31)$$

where  $h + gz$  is defined as the dry static energy. The above equations indicate (1) that enthalpy of a parcel decreases as it rises adiabatically because it is doing gravitational work, and (2) that the static energy (the sum of enthalpy and the gravitational potential energy) is conserved in an adiabatic motion (ascent or descent). Enthalpy is thus the specific internal energy plus the term  $pa$  that accounts for the work done by the parcel on the surroundings.

### • Potential temperature

Let us assume that there is a variable  $\theta$  defined by the relation  $\theta = ATp^{-\beta}$  where  $A$  and  $\beta$  are constants. By taking the logarithm on both sides we get  $\ln \theta = \ln A + \ln T - \beta \ln p$ . Then by differentiating we arrive at

$$d \ln \theta = d \ln T - \beta d \ln p.$$

Consider now the first law in the form  $c_p dT - adp = \delta q$  and divide it by  $T$ . Then with the help of the ideal gas we obtain

$$d \ln T - \frac{R}{c_p} d \ln p = \frac{\delta q}{c_p T}.$$

For  $\beta = R/c_p$  the above two equations combine to give

$$d \ln \theta = \frac{\delta q}{c_p T}. \quad (4.32)$$

For adiabatic processes  $\delta q = 0$  and thus  $d \ln \theta = 0$ . As such we should expect that in adiabatic processes there should exist a measure  $\theta$  which is conserved. This measure can be defined as follows.

From equation (4.24) we have

$$\frac{T}{p^k} = \frac{T_0}{p_0^k}$$

where  $k = (\gamma - 1)/\gamma = 1 - c_v/c_p = R/c_p = 0.286$  (for dry air). The state  $(T_0, p_0)$  can be taken as a reference state. As such we can choose  $p_0 = 1000$  mb and denote the corresponding temperature as  $T_0$ . The above equation is expressed as

$$T_0 = T \left( \frac{p_0}{p} \right)^k \quad (4.33)$$

or

$$T_0 = p_0^k T p^{-k}.$$

If we compare the above expression to  $\theta = ATp^{-\beta}$  we see that  $T_0 = \theta$  for  $A = p_0^k$  and  $\beta = k$ . We call  $\theta$  the potential temperature and we regard it as the temperature a parcel will have if it is compressed or expanded *adiabatically* from any state  $(T, p)$  to the 1000 mb level. It follows that the potential temperature remains invariant during an adiabatic process. Thus, under adiabatic conditions,  $\theta$  can be used as a tracer of air motion. On timescales for which a parcel can be considered as adiabatic, constant values of  $\theta$  track the motion of this parcel, which takes place on a surface of constant  $\theta$ . From equation (4.33) it is clear that the distribution of  $\theta$  in the atmosphere depends on the distribution of  $T$  and  $p$ . In the atmosphere  $dp/dz \gg dT/dz$  (just think that 5 km above the surface pressure decreases on the average from about 1000 mb to 500 mb while the temperature decreases from 288 K to 238 K). Therefore, surfaces of constant  $\theta$  tend to be like isobaric surfaces. Before, we saw that for an ascent (descent) the parcel's temperature must decrease (increase) owing to the work done by the parcel (by the surroundings). With the definition of potential temperature we can extend this statement to read as follows: during an adiabatic ascent (descent) the parcel's temperature must decrease (increase) but in such a proportion as to preserve the parcel's potential temperature. Note that equation (4.32) indicates that for non-adiabatic processes the change in the potential temperature is a direct measure of the heat exchanged between the parcel and its environment. As a result a non-adiabatic parcel will drift across potential temperature surfaces in proportion to the net amount of heat exchanged with its environment.

### Examples

- (4.1) One mole of a gas expands from a volume of 10 liters and a temperature of 300 K to (a) a volume of 14 liters and a temperature of 300 K and (b) a volume of 14 liters and a temperature of 290 K. What is the work done by the gas on the environment in each case?

- (a) According to the definition of work

$$W = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{nR^*T}{V} dV.$$

Since the temperature remains the same the above equation gives

$$W = nR^*T \ln \frac{V_2}{V_1} = 839 \text{ J}.$$

- (b) In this case  $T$  does not remain constant. As such it cannot be taken outside the integral and the above equation cannot be applied.

When  $T$  does not remain constant, in order to calculate the work done we must have the explicit function describing the path from  $i$  to  $f$  in the  $(p, V)$  diagram, not just  $i$  and  $f$ . An approximation to this would be to define a temperature  $\bar{T}$  or a pressure  $\bar{p}$  that satisfied the relationship

$$\int_{V_1}^{V_2} \frac{T dV}{V} \approx \bar{T} \int_{V_1}^{V_2} \frac{dV}{V}$$

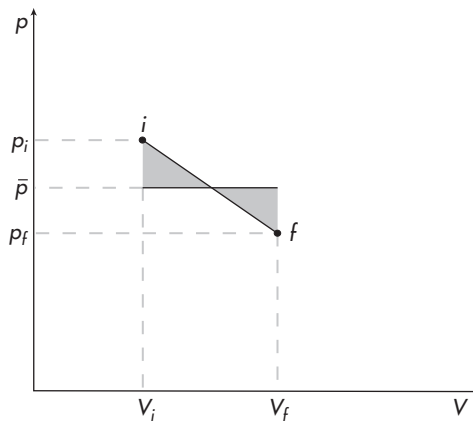
or the relationship

$$\int_{V_1}^{V_2} p dV = \bar{p} \int_{V_1}^{V_2} dV$$

Since in our case no clues are given about the function describing the path from  $i$  to  $f$  we are free to make (reasonable) assumptions. We can thus assume that  $i$  and  $f$  are connected by a straight line. From the data we can estimate that  $p_i = 249\,420$  Pa and  $p_f = 172\,200$  Pa. From Figure 4.6 it is easy to see that the work done is the area of the trapezoid  $ifV_fV_i$ . Because of the equality of the shaded triangles this area is equal to the area of the rectangle defined by the lines  $p = 0$ ,  $p = \bar{p}$ ,  $V = V_i$ ,  $V = V_f$  where  $\bar{p} = p_1 + p_2/2$ . Thus

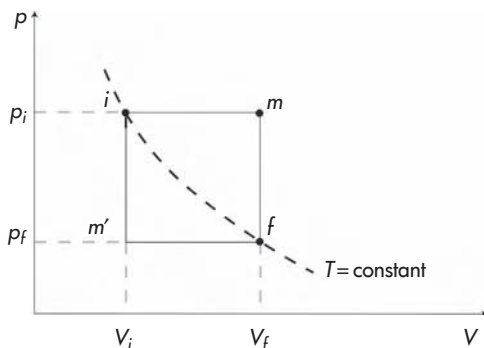
$$W = \bar{p}(V_f - V_i) = 843 \text{ J.}$$

**Figure 4.6**  
Diagram for example 4.1.



**Figure 4.7**

Diagram for example 4.2.



- (4.2) Consider an initial,  $i$ , and a final,  $f$ , state of a gas on an isotherm with  $V_f > V_i$ . The gas goes from  $i$  to  $f$  via an isobaric expansion and subsequent isochoric cooling; sketch on a  $(p, V)$  diagram the complete transformation and find the work done. If instead the gas goes from  $i$  to  $f$  via an isochoric cooling followed by an isobaric expansion, will the work done be different from before?

In the first case the gas goes from  $i$  to  $m$  (isobaric from  $V_i$  to  $V_f$ ) and then from  $m$  to  $f$  (isochoric from  $p_i$  to  $p_f$ ) (Figure 4.7). The total work done from  $i \rightarrow f$  will be the sum of the work done from  $i \rightarrow m$  and from  $m \rightarrow f$

$$\begin{aligned} W_1 &= \int_{V_i}^{V_f} p dV + \int_{V_f}^{V_f} p dV \\ &= p_i \int_{V_i}^{V_f} dV = p_i(V_f - V_i). \end{aligned}$$

In the second case the gas goes from  $i$  to  $m'$  (isochoric from  $p_i$  to  $p_f$ ) and then from  $m'$  to  $f$  (isobaric from  $V_i$  to  $V_f$ ). As before we have that the total work from  $i \rightarrow f$  is

$$\begin{aligned} W_2 &= \int_{V_i}^{V_i} p dV + \int_{V_i}^{V_f} p dV \\ &= p_f \int_{V_i}^{V_f} dV = p_f(V_f - V_i). \end{aligned}$$

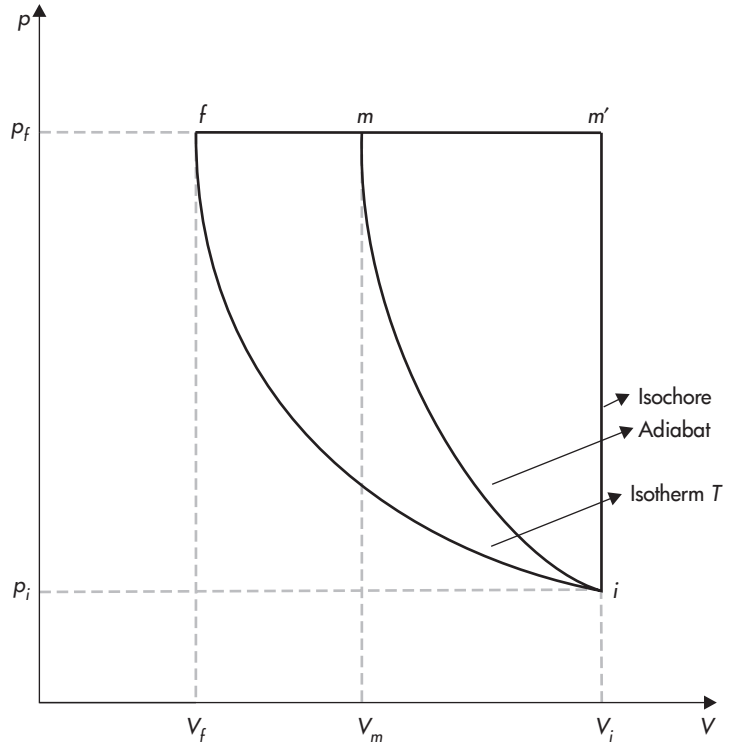
Since  $p_i \neq p_f$  it follows that  $W_1 \neq W_2$ .

- (4.3) Calculate  $Q, W$ , and  $\Delta U$  for the following processes (Figure 4.8):

- (a) isothermal reversible compression from state  $i = (p_i, V_i)$  to state  $f = (p_f, V_f)$ ;

**Figure 4.8**

Diagram describing the processes in example 4.3.



- (b) adiabatic reversible compression from state  $i = (p_i, V_i)$  to state  $m = (p_f, V_m)$  and a subsequent isobaric reversible compression to state  $f = (p_f, V_f)$ ;
- (c) reversible isochoric increase of the temperature from state  $i = (p_i, V_i)$  to state  $m' = (p_f, V_i)$  and a subsequent reversible isobaric decrease in temperature to state  $f = (p_f, V_f)$ .

Express all answers in terms of  $p_i, p_f$ , and  $T$ , where  $T$  is the temperature of the isotherm in (a).

- (a) During this transformation  $T_i = T_f = T, \Delta T = 0$  and  $\Delta U = 0$ . Then from the first law it follows that

$$\begin{aligned} Q = W &= \int_i^f p dV = nR^*T \int_i^f \frac{dV}{V} \\ &= nR^*T \ln \frac{V_f}{V_i} = nR^*T \ln \frac{p_i}{p_f}. \end{aligned}$$

- (b) This transformation consists of two branches ( $i \rightarrow m$  and  $m \rightarrow f$ ). From (a), the initial and final temperature is the same, i.e.  $\Delta U = 0$ . Thus, again we have

$Q = W$  with

$$\Delta U = \Delta U_{i \rightarrow m} + \Delta U_{m \rightarrow f}$$

$$Q = Q_{i \rightarrow m} + Q_{m \rightarrow f}$$

and

$$W = W_{i \rightarrow m} + W_{m \rightarrow f}.$$

Since the branch  $i \rightarrow m$  is adiabatic it follows that  $Q_{i \rightarrow m} = 0$  and

$$W_{i \rightarrow m} = -\Delta U_{i \rightarrow m} = -C_V(T_m - T_i). \quad (4.34)$$

$T_m$  and  $T_i$  are related via the equation

$$T_i p_i^{\frac{1-\gamma}{\gamma}} = T_m p_m^{\frac{1-\gamma}{\gamma}},$$

where  $p_m = p_f$ . It follows that

$$T_m = T_i \left( \frac{p_i}{p_f} \right)^{\frac{1-\gamma}{\gamma}} = T \left( \frac{p_i}{p_f} \right)^{\frac{1-\gamma}{\gamma}}.$$

Then from equation (4.34) we obtain

$$W_{i \rightarrow m} = -C_V T \left[ \left( \frac{p_i}{p_f} \right)^{\frac{1-\gamma}{\gamma}} - 1 \right]. \quad (4.35)$$

Branch  $m \rightarrow f$  is isobaric. Thus,

$$W_{m \rightarrow f} = \int_m^f p dV = p_f (V_f - V_m). \quad (4.36)$$

$V_m$  and  $V_i$  are related via Poisson's equation as follows

$$p_i V_i^\gamma = p_m V_m^\gamma.$$

Since  $p_m = p_f$  the above equation becomes

$$\left( \frac{V_m}{V_i} \right)^\gamma = \frac{p_i}{p_f}$$

or

$$V_m = V_i \left( \frac{p_i}{p_f} \right)^{1/\gamma}.$$

Then equation (4.36) can be written as

$$\begin{aligned} W_{m \rightarrow f} &= p_f \left[ V_f - V_i \left( \frac{p_i}{p_f} \right)^{1/\gamma} \right] \\ &= p_f V_f \left[ 1 - \frac{V_i}{V_f} \left( \frac{p_i}{p_f} \right)^{1/\gamma} \right] \end{aligned}$$

$$\begin{aligned}
&= nR^*T \left[ 1 - \frac{p_f}{p_i} \left( \frac{p_i}{p_f} \right)^{1/\gamma} \right] \\
&= nR^*T \left[ 1 - \left( \frac{p_i}{p_f} \right)^{\frac{1-\gamma}{\gamma}} \right] \quad (4.37)
\end{aligned}$$

From equations (4.35) and (4.37) it follows that overall

$$\begin{aligned}
Q = W &= -C_V T \left[ \left( \frac{p_i}{p_f} \right)^{\frac{1-\gamma}{\gamma}} - 1 \right] \\
&\quad + nR^*T \left[ 1 - \left( \frac{p_i}{p_f} \right)^{\frac{1-\gamma}{\gamma}} \right] \\
&= C_p T \left[ 1 - \left( \frac{p_i}{p_f} \right)^{\frac{1-\gamma}{\gamma}} \right].
\end{aligned}$$

- (c) Here also the transformation consists of two branches,  $i \rightarrow m'$  and  $m' \rightarrow f$ . Branch  $i \rightarrow m'$  is isochoric, so

$$W_{i \rightarrow m'} = 0.$$

Branch  $m' \rightarrow f$  is isobaric, which gives

$$W_{m' \rightarrow f} = \int_{m'}^f p dV = p_f (V_f - V_{m'}) = p_f (V_f - V_i)$$

or

$$\begin{aligned}
W_{m' \rightarrow f} &= p_f V_f \left( 1 - \frac{V_i}{V_f} \right) \\
&= nR^*T \left( 1 - \frac{p_f}{p_i} \right)
\end{aligned}$$

Here again  $T_i = T_f = T$ ,  $\Delta T = 0$  and  $\Delta U = 0$ .

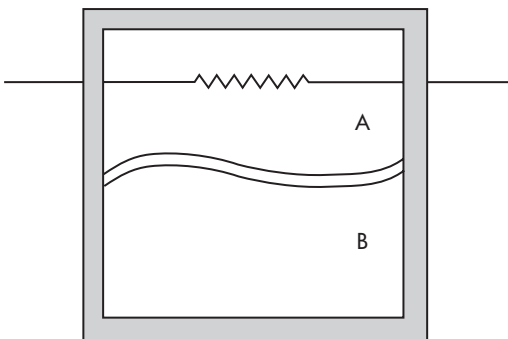
Thus, overall

$$Q = W = nR^*T \left( 1 - \frac{p_f}{p_i} \right).$$

- (4.4) This following problem is due to Iribarne and Godson (1973). Students should try to solve it before looking at the solution here. Figure 4.9 shows an insulated box with two compartments  $A$  and  $B$ . Both compartments contain a monatomic ideal gas and they are separated by a wall that on one hand does not allow any heat through it but on the other hand is flexible enough to ensure equalization of pressure in both compartments. The initial

**Figure 4.9**

Diagram for example 4.4.



conditions for both compartments are the same:  $T_i = 273 \text{ K}$ ,  $V_i = 1000 \text{ cm}^3$ , and  $p_i = 1 \text{ atmosphere}$  ( $1013 \times 10^2 \text{ Pa}$ ). Then, by means of an electrical resistance, heat is supplied to the gas in  $A$  until its pressure becomes ten times its initial pressure. Estimate: (a) the final temperature of the gas in  $B$ , (b) the work performed on the gas in  $B$ , (c) the final temperature of the gas in  $A$ , and (d) the heat absorbed by the gas in  $A$ .

- (a) The heat that is supplied to gas in  $A$  results in an increase in all its state variables. As it expands, it compresses the gas in  $B$  but it does not provide it with any of its heat because of the insulating wall between them. Since the wall is flexible the gas in  $B$  is compressed adiabatically until its pressure equals that inside compartment  $A$ . As such  $p_{Bf} = 10 \text{ atmospheres}$ . From Poisson's equation we can then solve for  $T_{Bf}$

$$T_{Bi} p_{Bi}^{\frac{1-\gamma}{\gamma}} = T_{Bf} p_{Bf}^{\frac{1-\gamma}{\gamma}}$$

Since the gas is monatomic  $\gamma = 1.666$ . Thus,

$$T_{Bf} = \left( \frac{p_{Bi}}{p_{Bf}} \right)^{-0.4} T_{Bi} \approx 686 \text{ K}.$$

Having  $T_{Bf}$  we can use the other form of Poisson's equation to find  $V_{Bf}$ :

$$T_{Bi} V_{Bi}^{\gamma-1} = T_{Bf} V_{Bf}^{\gamma-1}$$

or

$$\begin{aligned} V_{Bf} &= \left( \frac{T_{Bi}}{T_{Bf}} \right)^{1/\gamma-1} V_{Bi} = \left( \frac{273}{686} \right)^{1.5} V_{Bi} \\ &= 0.25 V_{Bi} = 250 \text{ cm}^3. \end{aligned}$$



- (b) The work performed on the gas in  $B$  is given by

$$W = -\Delta U = -C_V(T_{Bf} - T_{Bi}) = -413 C_V \text{ J.}$$

As we know, for a monatomic gas  $C_V = \frac{3}{2}nR^*$ . The number of moles  $n$  can be found from the ideal gas law and the initial conditions. It follows that

$$n = \frac{p_i V_i}{R^* T_i} = 0.0446 \text{ mol.}$$

Accordingly,  $C_V = 0.556 \text{ J K}^{-1}$  and

$$W \approx -230 \text{ J}$$

or

$$W \approx -55 \text{ cal.}$$

- (c) Since the final volume in  $B$  is  $250 \text{ cm}^3$  it follows that the final volume in  $A$  is  $1750 \text{ cm}^3$ . By applying the ideal gas law for the initial and final conditions in  $A$  we find that

$$T_{Af} = \frac{p_{Af} V_{Af}}{p_{Ai} V_{Ai}} T_{Ai} = 4777 \text{ K.}$$

- (d) The heat absorbed by the gas in  $A$  is given from the first law

$$Q = \Delta U + W.$$

Here  $W = 55 \text{ cal}$  (i.e. the opposite of the work done *on* gas  $B$ ), and  $\Delta U = C_V(T_{Af} - T_{Ai}) = 2504 \text{ J} = 598 \text{ cal}$ . Thus

$$Q = 598 + 55 = 653 \text{ cal.}$$

## Problems

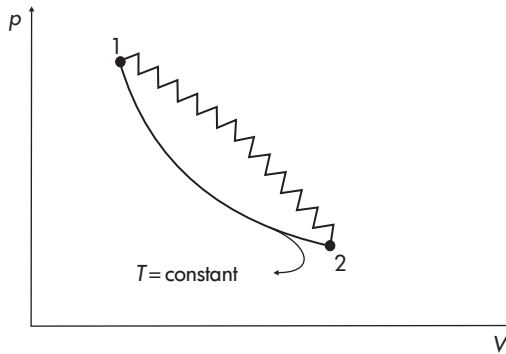
- (4.1) Commercial aircraft fly near  $200 \text{ mb}$  where typically the outside temperature is  $-60^\circ\text{C}$ . (a) Calculate the temperature of air if compressed adiabatically to the cabin pressure of  $1000 \text{ mb}$ . (b) How much specific heat must be added or removed (isobarically) to maintain the cabin at  $25^\circ\text{C}$ ? Consider the air as dry air. ( $337.5 \text{ K}$ ,  $9.5 \text{ cal g}^{-1}$  has to be removed)
- (4.2) A sample of  $100 \text{ g}$  of dry air has an initial temperature of  $270 \text{ K}$  and pressure  $900 \text{ mb}$ . During an isobaric process heat is added and the volume expands by  $20\%$  of its initial volume. Estimate: (a) the final temperature of the air, (b) the

amount of heat added, and (c) the work done against the environment. (324 K, 5427 J, 1550 J)

- (4.3) An air parcel moves from  $p_i$  to  $p_f$ . If its initial temperature is  $T_i$  find: (a) the specific work done by or on the parcel if its change happens adiabatically, (b) the specific work if its change happens isothermally, and (c) the change in the parcel's potential temperature in (a) and (b).
- (4.4) One mole of dry air has an initial state  $T = 273$  K and  $p = 1$  atmosphere. It undergoes a process in which its volume becomes four times its initial volume at 400 mb. If air is considered an ideal gas and if the process obeys the law  $pV^\eta = \text{constant}$ , estimate (a) the value of  $\eta$ , (b) the final temperature, (c) the change in internal energy, the work done, and the heat exchanged between the air and its surroundings. Look at your results carefully and elaborate on what kind of process would generate results like these. Is this process a realistic process? (0.67, 431 K, 3286 J, 3989 J, 7275 J)
- (4.5) Assume that you are on the top of a mountain at an altitude of 15 000 feet and there are no clouds above or below. If the temperature is  $-12^\circ\text{C}$  what will the temperature be at 3500 feet altitude? ( $22.4^\circ\text{C}$ )
- (4.6) A parcel of dry air has a volume 10 liters, a temperature  $27^\circ\text{C}$ , and a pressure 1 atmosphere. The parcel (a) is compressed isothermally until its volume becomes 2 liters, and (b) expands adiabatically until its volume becomes 10 liters. Describe these changes graphically in a  $(p, V)$  diagram. On it mark the values of  $p, V, T$  for each case.
- (4.7) A sample of dry air has a temperature of 300 K, a volume of 3 liters, and a pressure of 4 atmospheres. The air then undergoes the following changes: (a) it is warmed under a constant pressure to 500 K, (b) it is cooled under constant volume to 250 K, (c) it is cooled under constant pressure to 150 K, and (d) it is warmed under constant volume to 300 K. (1) Describe graphically on a  $(p, V)$  diagram each of the changes and mark on it the final values for pressure and volume after each change. (2) Calculate the total work done. (405.2 J)
- (4.8) For an ideal gas what on a  $(p, V)$  diagram describes the lines for which  $U = \text{constant}$ ?
- (4.9) An ideal gas undergoes two transformations from state 1 to state 2 which follow the two curves in Figure 4.10. In which of the transformations is (a) the change in internal energy greater? (b) the heat absorbed greater?
- (4.10) One kilogram of dry air is warmed from  $20^\circ\text{C}$  to  $70^\circ\text{C}$  under a constant pressure of 1 atmosphere. Calculate: (a) the heat

**Figure 4.10**

Diagram for Problem 4.9.



absorbed by the gas, (b) the work done, and (c) the change in internal energy. (50 250 J, 14 350 J, 35 900 J)

- (4.11) Hydrogen under  $p = 5$  atmospheres and  $T = 20^\circ\text{C}$  is warmed isobarically until its volume increases from 1 to 2 liters. Calculate the absorbed heat. (1773.4 J)
- (4.12) Inside a cylinder closed by a piston there is 88 g of an unknown diatomic gas of a temperature  $0^\circ\text{C}$ . The gas is then compressed adiabatically until its volume becomes equal to  $1/10$  of the initial volume. The change in internal energy is 17 158 J. Identify the gas. (Carbon dioxide)
- (4.13) Provide an example that proves that heat transfer is an irreversible process.
- (4.14) At  $T = 0^\circ\text{C}$  and  $p = 1000$  mb, 1 g of dry air receives during an isochoric process an amount of heat. It is then observed that its pressure increases by 50 mb. What is the change in the temperature of the air and what is the amount of heat absorbed? ( $13.6^\circ\text{C}$ , 2.33 cal)
- (4.15) Calculate the change in specific energy of an adiabatic parcel whose speed changes from  $10\text{ m s}^{-1}$  to  $25\text{ m s}^{-1}$ . ( $-262.5\text{ J kg}^{-1}$ )

