

4. Statistical physics and thermodynamics

As defined in the previous chapter, the entropy of an isolated equilibrium system is a function of its energy. If two bodies that are themselves in equilibrium, but not with each other, are subsequently placed in contact, the combined system will conserve the total energy since that is an additive property of the system as a whole. However experimentally it is observed the entropy of the combined system, once it achieves equilibrium, will *always* be higher than the sum of its parts. Other processes can be constructed that alter the thermodynamic states of a body (other than direct contact with another body) and in all such processes the total entropy either increases or, at best, remains constant. Processes in which the entropy remains constant are said to be *reversible processes*, and those in which it increases are termed *irreversible*. Because of this property, a system is in equilibrium only if its entropy is a maximum.

4.1. Temperature

Consider a system that consists of two parts, 1 and 2. The total energy, being additive, is then

$$E^{\text{total}} = E^{(1)} + E^{(2)}. \quad (4.1)$$

If this system undergoes a process in which the total energy remains constant but that of the parts exchange some small amount of energy then Eq. (4.1) requires

$$dE^{(1)} = -dE^{(2)}. \quad (4.2)$$

Likewise the entropy is additive so

$$S^{\text{total}}(E^{\text{total}}) = S^{(1)}(E^{(1)}) + S^{(2)}(E^{(2)}). \quad (4.3)$$

We now ask what is required for the two bodies to be in equilibrium. From the above discussion this requires total entropy be a maximum. Maximizing S^{total} with respect to $E^{(1)}$ while imposing the constraint implied by Eq. (4.2) then gives

$$\begin{aligned} \frac{dS^{\text{total}}}{dE^{(1)}} &= \frac{dS^{(1)}}{dE^{(1)}} + \frac{dS^{(2)}}{dE^{(2)}} \frac{dE^{(2)}}{dE^{(1)}} \\ &= \frac{dS^{(1)}}{dE^{(1)}} - \frac{dS^{(2)}}{dE^{(2)}} = 0, \end{aligned}$$

or equivalently

$$\frac{dS^{(1)}}{dE^{(1)}} = \frac{dS^{(2)}}{dE^{(2)}}. \quad (4.4)$$

This argument can be extended to multiple bodies and we therefore reach the conclusion that the derivative of S with respect to E must be *constant* for various parts of a system that is in equilibrium; the reciprocal of this quantity, dS/dE , is called the *absolute temperature* and designated as T :

$$\frac{1}{T} = \frac{dS}{dE}. \quad (4.5)$$

We see that temperature, being defined via the entropy, only has a *statistical* meaning (through the entropy which itself is defined statistically). Bodies with larger temperatures are said to be *hotter*; those with smaller temperatures are said to be *colder*.

Consider two bodies that are not in equilibrium with each other but which are subsequently brought into contact. The total entropy then increases with time according to

$$\frac{dS^{\text{total}}}{dt} = \frac{dS^{(1)}}{dE^{(1)}} \frac{dE^{(1)}}{dt} + \frac{dS^{(2)}}{dE^{(2)}} \frac{dE^{(2)}}{dt}.$$

Using the definition (4.5) followed by the condition (4.2) we obtain

$$\begin{aligned} \frac{dS^{\text{total}}}{dt} &= \frac{1}{T^{(1)}} \frac{dE^{(1)}}{dt} + \frac{1}{T^{(2)}} \frac{dE^{(2)}}{dt} \\ &= \frac{dE^{(1)}}{dt} \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) > 0. \end{aligned} \quad (4.6)$$

So $E^{(1)}$ will increase in time if its temperature is lower: *energy flows from hotter bodies to colder bodies* and never the other way.

4.2. Adiabatic processes

In mechanics one introduces the concept of an adiabatic change. There one finds that certain quantities in a system, called *actions*, are invariant under a slow change in some parameter affecting the motion¹, the requirement being that the rate of change of that parameter be slow, say when measured against some oscillatory period or characteristic relaxation time of the system. This concept carries over into thermodynamics.

We write the Hamiltonian of our system as $H = H(p, q; \lambda(t))$ where p, q and t denote the Hamiltonian coordinates of the particles making up the system, and we have designated the time dependent parameter as $\lambda(t)$. We now examine the behavior of the entropy of the system

¹ In practice, and depending on the system, multiple parameters may be present.

governed by this Hamiltonian. We expand the rate of change of the entropy in a power series in $d\lambda(t)/dt$ as

$$\frac{dS}{dt} = C_0 + C_1 \frac{d\lambda}{dt} + C_2 \left(\frac{d\lambda}{dt} \right)^2 + \dots \quad (4.7)$$

The first term vanishes because the entropy is constant in equilibrium and the second term vanishes because the entropy is also a maximum. Hence our expansion begins with the second order term. Using the chain rule together with (4.7) we can write

$$\frac{dS}{dt} = \frac{dS}{d\lambda} \frac{d\lambda}{dt} = C_2 \left(\frac{d\lambda}{dt} \right)^2$$

or

$$\frac{dS}{d\lambda} = C_2 \frac{d\lambda}{dt}, \quad (4.8)$$

which approaches zero as $d\lambda/dt \rightarrow 0$. Hence the entropy is conserved under changes in λ provided they are carried out *sufficiently slowly*. Furthermore we can change the sign $d\lambda/dt \rightarrow -d\lambda/dt$ and in so doing return a system to its original state; i.e., purely *adiabatic processes are reversible*.

Often the parameter λ is some macroscopic variable having no simple microscopic meaning, examples being a pressure or volume change carried out on a mechanical system. But no process can be carried out infinitely slowly and in any case will depend on the details of what contributes to the parameter C_2 in Eq. (4.8). So the entropy always increases at some level. This *entropy increase* (or the entropy so “generated”) is a *universal property of Nature*. It forms an implicit part of what makes up the *second law of thermodynamics*.

We now examine the effect of a change in our parameter λ with time on the total energy. From the Hamiltonian equation, $dH/dt = \partial H/\partial t$, and identifying H with E , we can write the total derivative of the *mechanical* energy as

$$\frac{dE(p,q;\lambda(t))}{dt} = \frac{\partial E(p,q;\lambda(t))}{\partial t} = \frac{\partial E(p,q;\lambda(t))}{\partial \lambda} \frac{d\lambda}{dt};$$

here we are regarding $\lambda(t)$ as the *explicit* time dependence in the Hamiltonian. To examine the thermodynamic response we must average this equation which gives

$$\left(\frac{dE(p,q;\lambda(t))}{dt} \right) = \left(\frac{\partial E(p,q;\lambda(t))}{\partial t} \right) = \frac{\partial E(p,q;\lambda(t))}{\partial \lambda} \frac{d\lambda}{dt}$$

where we interchanged time differentiation and time averaging. If we assume the change in λ is carried out adiabatically, where we can identify $\bar{E}(\lambda(t))$ with a thermodynamic energy $E(S, \lambda(t))$, we can write this last equation as

$$\frac{dE(S, \lambda)}{dt} = \left(\frac{\partial E}{\partial \lambda} \right)_S \frac{d\lambda}{dt}; \quad (4.9)$$

for the change at constant S , with the corresponding differential being $\delta E = (\partial \bar{E}(\lambda) / \partial \lambda)_S \delta \lambda$. This important formula tells us that we can calculate the change in energy of a system arising from a *slow change* in λ , from the *purely statistical* dependence of the energy on λ at fixed entropy.

To be clear, what we have established here is that the thermodynamic energy, rather than involving a single variable S as in section 4.1, now involves the *two* independent variables, S and λ . The full differential change is then written

$$\delta E = \left(\frac{\partial E}{\partial S} \right)_\lambda \delta S + \left(\frac{\partial E}{\partial \lambda} \right)_S \delta \lambda \quad (4.10)$$

or on dividing by δt

$$\frac{\delta E}{\delta t} = \left(\frac{\partial E}{\partial S} \right)_\lambda \frac{\delta S}{\delta t} + \left(\frac{\partial E}{\partial \lambda} \right)_S \frac{\delta \lambda}{\delta t}. \quad (4.11)$$

In examining the first term on the right hand side of (4.10) we recall that in earlier obtaining Eq. (4.5) we were implicitly holding external conditions constant, so we will now redefine our temperature as

$$(\partial E / \partial S)_\lambda = T. \quad (4.13)$$

The remaining derivative in (4.10) will be examined below.

4.3. Pressure, volume, work, and the thermodynamic identity

In our use of the word *system* to represent a group of particles we have avoided any discussion as to how close they are to each other in space. At the simplest level there will be a characteristic number of particles per unit volume, the so called *number density*², n . The separation between the particles would then scale as $n^{-1/3}$.

² If we associate a mass, m , with the particles, the number density, $n(\mathbf{r}, t)$, can be written in terms of the mass density as $\rho(\mathbf{r}, t) = m n(\mathbf{r}, t)$.

We are familiar with the three common forms, also called phases, of matter: gas, liquid, and solid. In the latter two phases, also called condensed phases, n is large and the separation between the particles arises from a balance (cancellation) of attractive (at longer range) and repulsive (at shorter range) forces acting between the molecules and/or atoms making them up. Now the range of the forces that act between particles (both attractive and repulsive) is typically of order a few Angstroms, i.e., of order the size of the participating particles themselves. In the region where the force balancing occurs, the molecules are tightly clumped together; the overall potential energy is then strongly negative and greatly exceeds the kinetic energy. Condensed phases spontaneously maintain some large number density with $n \sim 10^{22} / \text{cm}^3$ for terrestrial matter with corresponding spacings $n^{-1/3} \sim 10^{-7} \text{cm}$.

The energy of a liquid is independent of its shape, a property that allows it to flow; in the presence of gravity one usually confines it in a container. On the other hand solids resist a change in their shape, although they may, depending on their history, have any shape; *changing* that shape, while keeping the volume constant, requires external “shearing” forces (more correctly shear stresses). For this reason we will avoid a discussion of solids here.

For a gas the range of the inter particle force is typically much smaller than the spacing between particles, $n^{-1/3}$, in which case the total kinetic energy greatly exceeds the potential energy. If the number density remains constant the total energy will then scale with the amount of material, i.e., with the volume V of the gas, and would primarily involve the kinetic energy which on a per particle basis is largely independent of the density. If the gas density becomes high enough that $n^{-1/3}$ approaches the range of the inter particle forces, then the energy will have a contribution arising from both the kinetic and potential energies. But because the kinetic energy is generally dominant, any material in a gas phase will, left to itself, *disperse* and hence container walls are required to confine it.

In all cases, whether the statistical energy involves the volume through both the kinetic and potential energies (in condensed phases or a dense gas) or the kinetic energy alone (for a dilute gas) it is written $\overline{E(p,q;V)}$ where V functions as the *external parameter* λ that was discussed in section 4.2.

The time averaged impulses associated with molecular impacts on some wall that confines a gas results in an average force perpendicular to that wall; in equilibrium it must be

counter-balanced by an equal and opposite force that confines the gas. The confining force typically arises from the rigidity of the vessel containing the gas.

In the vessel shown in Fig. 4.1 we consider a special case where we introduce a *moveable wall*, called a *piston*, that slides in a leak-tight, friction-free fashion within the remainder of the confining chamber. To maintain equilibrium one must now apply an *external force* F to maintain the position of that wall. (The remaining walls still being held in place by the rigidity of the container.)

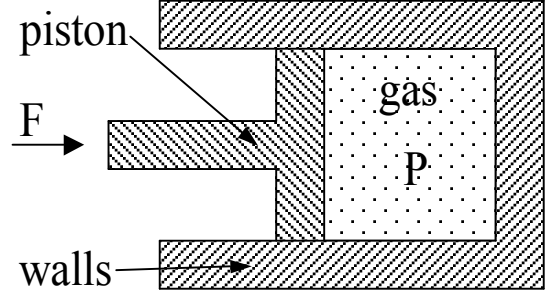


Fig. 4.1. A chamber with three fixed walls, confining a gas at pressure P , together with a moveable wall, a piston of area A , to which a force F is applied that allows displacing the piston by a length dL that causes a volume change $dV = A \cdot dL$.

If the piston is now displaced by an amount dL a work $dR = F \cdot dL$ will be performed. We now introduce the concept of pressure, P , which is defined as the *force per unit area*, F / A . The displacement dL results in a volume change $dV = A \cdot dL$. Combining these relations the differential work can then be written

$$dR = -PdV. \quad (4.13)$$

Having identified our external parameter as V we can write the thermodynamic energy as $E = E(S, V)$. If the entropy is held constant the differential work dR performed in compressing the material goes directly into increasing the internal energy; hence

$$(\partial E / \partial V)_S = -P. \quad (4.14)$$

Inserting (4.14) and (4.13) in Eq. (4.10) becomes

$$dE = TdS - PdV. \quad (4.15)$$

Eq. (4.14) is referred to the *thermodynamic identity*.³ From the above arguments it is clear that (4.15) applies only to *reversible* differential changes.

In the above expression involving $dR = -PdV$ we can regard P as a kind of *generalized force* and dV as a *generalized differential displacement*. In other systems, examples being those having electric or magnetic degrees of freedom, one defines alternate forces and differential displacements that contribute to the differential work dR . With this in mind we rewrite (4.15) in a more general form as

³ It is also a differential statement of the *combined first and second law of thermodynamics* in that it combines: i) conservation of energy and ii) conservation of entropy (for reversible processes).

$$dE = TdS + dR . \quad (4.16)$$

With our definition, the differential work, dR , is greater than zero if the energy of the system increases (where one says work is done *on* the system) and less than zero if the system energy decreases (where the system does work on the environment). Eq. (4.16) is viewed as the *generalized thermodynamic identity*.

4.4. Heat and work

Experimentally, we can carry out a differential increase in the energy, dE , of the system energy, E , by two independent mechanisms: i) cause some increment of energy, called heat and designated dQ , to pass from the surrounding environment into the system (say through its surface which requires the external environment have a higher temperature) or ii) cause a body in the outside world to do an increment of work, dR , on the system. Combining these we have

$$dE = dQ + dR \quad (4.17a)$$

where, depending on the process, the differentials can have either sign. From conservation of energy this relation must *always* be obeyed; i.e., reversibility is not assumed; it constitutes what is called the *first law of thermodynamics*⁴. In thermodynamic texts (4.17a) is more commonly written as

$$dQ = dE - dR . \quad (4.17b)$$

Now dE , is the differential of a thermodynamic function, e.g., $E(S,V)$. However dQ is *not* the derivative of some thermodynamic “Q function”; similarly dR is not the derivative of a “work function”⁵. One then says that dQ and dR are not *exact differentials*⁶. In particular, a change in the internal energy of the system involves contributions from an applied heat increment dQ and an increment of work, dR , and only their *sum* goes into changing the internal energy of the system.

If we write $dQ = TdS$ ⁷ which implies we are going along some chosen path *adiabatically* (*reversibly*), together with $dR = -PdV$, Eq. (4.17a) becomes identical to Eq. (4.15); here all

⁴ Historically it was established experimentally independent of mechanical considerations.

⁵ Said somewhat differently, there is no such thing as a thermodynamic Q or R function.

⁶ For this reason they are sometimes written as δQ and δR .

⁷ One sometimes says that T is an “integrating factor” that permits writing dQ for a reversible process as TdS where T and S are both thermodynamic variables in the system.

variables that enter are thermodynamic quantities⁸. The restriction of only traversing reversible paths results in unique outcomes that can be computed on the basis of thermodynamic quantities alone. What makes this possible is the presence of a *separately* conserved quantity, the entropy, which strongly constrains how the system can evolve along a chosen path, say in the space of P and V (as in certain heat engines).

The addition of heat increments dQ always occurs over some time interval dt . For cases where $dR = -PdV$ Eq. (4.17b) then gives us the time evolution equation

$$\frac{dQ}{dt} = \frac{dE}{dt} + P \frac{dV}{dt}.$$

If dQ/dt is kept small enough that the system evolves reversibly then we can write $dQ = TdS$ and this equation can be written as

$$\frac{dE}{dt} = T \frac{dS}{dt} + P \frac{dV}{dt};$$

comparing these last two equations we have

$$\frac{dQ}{dt} = T \frac{dS}{dt}. \quad (4.18)$$

However even when mechanical equilibrium is maintained, the system may not be in *complete* thermal equilibrium, e.g., when irreversible chemical reactions can occur (the rate of which increases with temperature); Eq. (4.18) is then replaced by an *inequality*

$$\frac{dQ}{dt} < T \frac{dS}{dt}. \quad (4.19)$$

4.5. The heat capacity

A readily measured property of a thermodynamic system is the change of temperature, ΔT , that results from the application of an increment of heat, ΔQ , from which we can form the ratio $C = \lim_{\Delta Q \rightarrow 0} (\Delta Q / \Delta T)$. This quantity is called the *specific heat* or the *heat capacity*. When the heat increments are added reversibly we can write $dQ = TdS$. However this ratio depends on how the experiment is performed. Two different conditions are commonly imposed: i) keep the

⁸ Eq. (4.16) is regarded as a statement of the combined first and second laws of thermodynamics, the first law being conservation of energy as given by (4.17a) and second being the existence of an entropy function together along with the concept of reversible paths leading to the expression $dQ = TdS$.

volume constant, and ii) keep the pressure constant. For the first of these, for which no work is performed, we have

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V \quad (4.20a)$$

$$= \left(\frac{\partial E}{\partial T} \right)_V \quad (4.20b)$$

where the second form follows immediately from Eq. (4.15). For the second case we have

$$C_P = T \left(\frac{\partial S}{\partial T} \right)_P \quad (4.21a)$$

$$= \left(\frac{\partial W}{\partial T} \right)_P \quad (4.21b)$$

where the second form comes from Eq. (4.23) which is obtained immediately below. Since we must account for the work the system does on the environment, which requires larger heat increments, we always have $C_P > C_V$.

4.6. Alternate thermodynamic potentials; Maxwell relations

From our discussion up to this point we see that the *statistical* energy, E , as it enters thermodynamics is most naturally defined as a function of S and V : $E = E(S, V)$. Once the absolute temperature scale is established, T is a readily measurable quantity whereas determining S is more subtle. For this reason it is important to have differential relations analogous to Eq. (4.15) that replace differentials of either or both of S and V with differentials of P and T that are valid for reversible processes. This can be done by performing what is called a *Legendre transformation*. Suppose we introduce a new function

$$W = E + PV \quad (4.22)$$

called the *enthalpy* or *heat function*. Writing the differential (4.22) in terms of differentials of its defining variables in first order we obtain

$$dW = dE + VdP + PdV.$$

Eliminating dE using Eq. (4.15) we have

$$dW = TdS - PdV + VdP + PdV$$

or

$$dW = TdS + VdP \quad (4.23)$$

The differential of this alternate thermodynamic function, $W(S,P)$, now involves dS and dP rather than dS and dV (as was the case for E). Proceeding in a similar way we can replace dS by dT by introducing two additional thermodynamic potentials according to the definitions

$$F = E - TS, \quad (4.24)$$

called the (Helmholtz) free energy, and

$$\Phi = E + PV - TS, \quad (4.25a)$$

or equivalently

$$\begin{aligned} \Phi &= F + PV \\ &= W - TS, \end{aligned} \quad (4.25b,c)$$

called the Gibbs free energy (or thermodynamic potential)⁹.

Taking the differential of these two functions and substituting (4.15) in the first and both (4.15) and (4.23) in the second we obtain

$$dF = -SdT - PdV \quad (4.26)$$

and

$$d\Phi = -SdT + VdP. \quad (4.27)$$

We now have two more thermodynamic functions, $F = F(T,V)$ and $\Phi = \Phi(T,P)$, but now expressed in terms of differentials of V and P . Collecting the first order expansions of these four thermodynamic potentials together we have

$$dE = \left(\frac{\partial E}{\partial S}\right)_V dS + \left(\frac{\partial E}{\partial V}\right)_S dV \quad (4.28a)$$

$$dW = \left(\frac{\partial W}{\partial S}\right)_V dS + \left(\frac{\partial W}{\partial P}\right)_S dP \quad (4.28b)$$

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV \quad (4.28c)$$

and

$$d\Phi = \left(\frac{\partial \Phi}{\partial T}\right)_P dT + \left(\frac{\partial \Phi}{\partial P}\right)_T dP. \quad (4.28d)$$

Comparing (4.28a) to (4.15) we obtain,

⁹ F and Φ are sometimes designated as A and G respectively in other treatments.

$$\left(\frac{\partial E}{\partial S}\right)_V = T \text{ and } \left(\frac{\partial E}{\partial V}\right)_S = -P. \quad (4.29a,b)$$

In a similar manner we can compare (4.28b) to (4.23), (4.28c) to (4.26), and (4.28d) to (4.27) to obtain

$$\left(\frac{\partial W}{\partial S}\right)_V = T; \quad \left(\frac{\partial W}{\partial P}\right)_S = V \quad (4.30a,b)$$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S; \quad \left(\frac{\partial F}{\partial V}\right)_T = -P \quad (4.31a,b)$$

and

$$\left(\frac{\partial \Phi}{\partial T}\right)_P = -S; \quad \left(\frac{\partial \Phi}{\partial P}\right)_T = V. \quad (4.32a,b)$$

When E , W , F , and Φ are continuous, the second derivatives with respect to both of their variables will be independent of the order. Applying this requirement to our four thermodynamic potentials we obtain

$$\frac{\partial^2 E}{\partial S \partial E} = \frac{\partial^2 E}{\partial E \partial S} \rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad (4.33a)$$

$$\frac{\partial^2 E}{\partial S \partial E} = \frac{\partial^2 E}{\partial E \partial S} \rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad (4.33b)$$

$$\frac{\partial^2 E}{\partial S \partial E} = \frac{\partial^2 E}{\partial E \partial S} \rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (4.33c)$$

and

$$\frac{\partial^2 E}{\partial S \partial E} = \frac{\partial^2 E}{\partial E \partial S} \rightarrow \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P; \quad (4.33d)$$

these four identities are commonly called the *Maxwell relations*, and as we will see shortly are very useful in that they allow us to replace derivatives that would be hard to measure experimentally with ones that are more readily available.

Given any one of our four potentials we can construct any of the remaining three. As an example, with $F = E - TS$ defined by Eq. (4.24) and $S = -(\partial F / \partial T)_V$ from (4.31a) we obtain

$$F = E + T(\partial F / \partial T)_V \text{ or}$$

$$E = F - T(\partial F / \partial T)_V \quad (4.34)$$

with E now expressed in terms of the independent variables of F ; i.e. we obtain $E = E(T, V)$, rather than $E = E(S, V)$.

4.7. Changing the constrained variable on a partial derivative

A commonly occurring problem that arises in thermodynamics is relating partial derivatives in which different quantities are held constant. As an example we now relate the functions C_P and C_V introduced in Eq.'s (4.20) and (4.21). This is most easily accomplished using some properties of quantities called *Jacobians*¹⁰ defined as

$$\frac{\partial(u, v)}{\partial(x, y)} \equiv \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix} = \frac{\partial u}{\partial x} \frac{\partial v}{\partial y} - \frac{\partial u}{\partial y} \frac{\partial v}{\partial x} \quad (4.35)$$

where $u = u(x, y)$ and $v = v(x, y)$. From this definition we immediately have

$$\frac{\partial(u, v)}{\partial(x, y)} = -\frac{\partial(v, u)}{\partial(x, y)} = -\frac{\partial(u, v)}{\partial(y, x)}. \quad (4.36)$$

Furthermore

$$\frac{\partial(u, y)}{\partial(x, y)} = \frac{\partial u}{\partial x} \frac{\partial y}{\partial y} - \frac{\partial u}{\partial y} \frac{\partial y}{\partial x} = \left(\frac{\partial u}{\partial x} \right)_y \quad (4.37)$$

where we exploited the property that x and y are independent variables. Finally Jacobians obey a generalized chain rule

$$\frac{\partial(u, v)}{\partial(x, y)} = \frac{\partial(u, v)}{\partial(s, t)} \frac{\partial(s, t)}{\partial(x, y)}. \quad (4.38)$$

Returning to the problem of relating the heat capacities at constant V and P we write

$$\begin{aligned} \left(\frac{\partial S}{\partial T} \right)_V &= \frac{\partial(S, V)}{\partial(T, V)} = \frac{\partial(S, V)}{\partial(T, P)} \frac{\partial(T, P)}{\partial(T, V)} \\ &= \left[\left(\frac{\partial S}{\partial T} \right)_P \left(\frac{\partial V}{\partial P} \right)_T - \left(\frac{\partial S}{\partial P} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \right] \left(\frac{\partial P}{\partial V} \right)_T. \end{aligned}$$

Writing $(\partial P / \partial V)_T = (\partial V / \partial P)_T^{-1}$ we have

¹⁰ As we will see Jacobians greatly simplify the interrelation of derivatives encountered in thermodynamics and it is worth the effort to become familiar with them.

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial T}\right)_P - \frac{(\partial S / \partial P)_T (\partial V / \partial T)_P}{(\partial V / \partial P)_T}$$

and using the Maxwell relation $(\partial S / \partial P)_T = -(\partial V / \partial T)_P$ given by Eq. (4.33d) we obtain

$$C_V - C_P = T \frac{(\partial V / \partial T)_P^2}{(\partial V / \partial P)_T}. \quad (4.39)$$

The quantities $(\partial V / \partial T)_P$ and $(\partial V / \partial P)_T$ are related to the *thermal expansion* and the *compressibility* respectively (see section 4.11), which are experimental properties that can be measured independently.

We will also examine the derivative $(\partial V / \partial P)_S$ which is related to the velocity of sound waves which travel adiabatically

$$\begin{aligned} \left(\frac{\partial V}{\partial P}\right)_S &= \frac{\partial(V, S)}{\partial(P, S)} = \frac{\partial(V, S)}{\partial(V, T)} \frac{\partial(V, T)}{\partial(P, T)} \frac{\partial(P, T)}{\partial(P, S)} \\ &= \frac{(\partial S / \partial T)_V}{(\partial S / \partial T)_P} \left(\frac{\partial V}{\partial P}\right)_T = \frac{C_V}{C_P} \left(\frac{\partial V}{\partial P}\right)_T. \end{aligned} \quad (4.40)$$

Since $C_P > C_V$ the adiabatic sound velocity (constant S) is greater than the isothermal sound velocity.

4.8. Writing extensive quantities as specific quantities

The additivity of E and S, and with it our alternate potentials W, F, and Φ , implies that these quantities are proportional to (scale with) the amount of material in our system. For conventional matter this is the number of particles, N, or the mass, M, of our system. Therefore it is common divide extensive quantities by one of these variables; such quantities are called *specific quantities*. Here we will divide by the particle number and rewrite our potentials in terms of quantities per particle. As an example consider the energy

$$E = Ne(S / N, V / N) = Ne(s, v), \quad (4.41a)$$

where $e = E / N$, $s = S / N$, and $v = V / N$. Mathematically one says that E is a homogeneous function of first order in N, S, and V. Proceeding in a similar way with the remaining thermodynamic potentials we have

$$W = Nw(s, P), \quad (4.41b)$$

$$F = Nf(T, v) \quad (4.41c)$$

and

$$\Phi = N\phi(T,P) \quad (4.41d)$$

although ϕ is more commonly denoted as μ (see below).

In chemistry it is common to introduce quantities *per mole*, a mole (denoted mol) being defined as the value of Avogadro's number, $\mathcal{A}_0 = 6.0221 \times 10^{23}$, of the particles (atoms or molecules) of some material. A gram molecular weight (a gram mole) would then be $\mathcal{A}_0 \times m$ where m is the mass of the atom or molecule under consideration.¹¹

4.9. Incorporating the particle number into the thermodynamic potentials

We now extend the thermodynamic identity so as to directly include a dependence on the number of particles

$$dE = TdS - PdV + \mu dN \quad (4.42a)$$

where we have introduced a new intensive parameter, μ , called the *chemical potential*; here it would be determined through a measurement of the change in energy with particle number¹² at constant S and V

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{S,V} . \quad (4.43a)$$

Since the additional term in (4.42a) does not affect the Legendre transformations used to construct the remaining thermodynamic potentials, the added dependence on particle number enters in the same way in the other three potentials

$$dW = TdS + VdP + \mu dN , \quad (4.42b)$$

$$dF = -SdT - PdV + \mu dN , \quad (4.42c)$$

and

$$d\Phi = SdT + VdP + \mu dN , \quad (4.42d)$$

with μ calculated as follows

$$\mu = \left(\frac{\partial W}{\partial N} \right)_{S,P} , \quad \mu = \left(\frac{\partial F}{\partial N} \right)_{T,V} , \quad \mu = \left(\frac{\partial \Phi}{\partial N} \right)_{T,P} . \quad (4.43b-d)$$

¹¹ Strictly speaking this would be an average over the abundance of the isotopes of the atoms making up the molecule. Suppressing the nuclear binding energy it can be approximated by the adding the masses of all the neutrons and protons of all the atoms making up the molecule.

¹² Designing ways to experimentally do this in a *reversible* manner can be a challenge.

Since Φ is a function of T, P , and N , (4.43d) can be directly integrated to give

$$\Phi(T, P, N) = N\mu(T, P). \quad (4.44)$$

Directly differentiating (4.44) gives

$$d\Phi = d(\mu N) = Nd\mu + \mu dN;$$

equating this with Eq. (4.42d) and dividing through by N we obtain

$$d\mu = -sdT + vdP \quad (4.45)$$

where we substituted the specific entropy and volume introduced after Eq. (4.41). This equation is often referred to as the *Gibbs-Duham relation*.

Having introduced N as an independent variable it is useful in many applications to introduce yet another thermodynamic potential, the omega potential

$$\Omega = F - \mu N = F - \Phi = -PV. \quad (4.46)$$

Differentiating Ω in the form $F - \mu N$ and substituting Eq. (4.42c) gives

$$d\Omega = -SdT - PdV + \mu dN - Nd\mu - \mu dN$$

or

$$d\Omega = -SdT - PdV - Nd\mu. \quad (4.47)$$

From (4.47) we obtain

$$N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V}. \quad (4.48)$$

Recalling $\Omega = -PV$ and combining (4.47) and (4.48) gives

$$N = V\left(\frac{\partial P}{\partial \mu}\right)_{T, V}. \quad (4.49)$$

As we will discuss in more detail in a later chapter, the contribution $-Nd\mu$ that we have added to the differentials of the thermodynamic potentials can be generalized to the case where there are multiple particle species by replacing $-Nd\mu$ with $-\sum_{i=1}^n N_i d\mu_i$ where i numbers the n different chemical species present.

4.10. Particle number equilibrium between bodies in contact

Suppose two bodies that can exchange particles are placed in contact, and that the total particle number N remains constant. Writing $N = N_1 + N_2 = \text{const.}$ we then have

$$dN_1 = -dN_2. \quad (4.50)$$

We write the entropy of the two bodies as $S = S_1(N_1) + S_2(N_2)$ and require that in equilibrium it be a maximum with respect to either of the particle numbers. Choosing this as N_1 we have

$$\begin{aligned} 0 &= \frac{\partial S}{\partial N_1} = \frac{\partial S_1}{\partial N_1} + \frac{\partial S_2}{\partial N_1} = \frac{\partial S_1}{\partial N_1} + \frac{\partial S_2}{\partial N_2} \frac{dN_2}{dN_1} \\ &= \frac{\partial S_1}{\partial N_1} - \frac{\partial S_2}{\partial N_2} \end{aligned}$$

telling us that

$$\frac{\partial S_1}{\partial N_1} = \frac{\partial S_2}{\partial N_2}. \quad (4.51)$$

If in performing this experiment the overall volume and energy are held constant then from Eq. (4.42a) we would conclude

$$\left(\frac{\partial S}{\partial N} \right)_{E,V} = -\frac{\mu}{T}. \quad (4.52)$$

Equilibrium requires the temperatures of the two bodies be the same and on combining Eq.'s (4.51) and (4.52) we obtain the condition for equilibrium with respect to particle number to be¹³

$$\mu_1 = \mu_2. \quad (4.53)$$

Hence two subsystems are in equilibrium with respect to their particle numbers when their chemical potentials are equal. As noted above we will later generalize this condition to the case where multiple particle species are present.

4.11. Thermodynamic response functions

We now discuss some additional properties that are used to characterize thermodynamic systems. In all cases they involve the change (or response) of some dependent variable to a change in a convenient independent variable.

Thermodynamic variables differ with respect to how easy they are to measure. Under many conditions one can conveniently measure temperature, pressure and mass; the technology to construct thermometers, pressure gauges, and mass balances is well developed. Measuring volume, particle number, chemical potential, etc. is more challenging.

In section 4.5 we introduced the heat capacity which is a measure of how much heat ΔQ is needed to raise the temperature by an amount ΔT , $\Delta Q \equiv C\Delta T$. As emphasized there, the heat

¹³ This relation is useful when describing a liquid in equilibrium with a gas of its own particles.

capacity depends on the conditions maintained during the experiment. If the volume is held constant the heat capacity is

$$(dQ / dT)_V = (\partial E / \partial T)_V = T(\partial S / \partial T)_V .$$

The heat needed is smaller than when performing the experiment at constant pressure where the system does work on the environment which resulted in $C_P > C_V$.

Historically heat increments ΔQ were measured in terms of the temperature change they induced in a standard material, chosen as water: they were measured in units of *calories* where a calorie was defined as the amount of heat needed to change the temperature of one gram of water by one degree centigrade¹⁴. Our development has been based on mechanical energy increments, typically joules (MKS) or ergs (cgs). Historically the connection between these units was established by James Prescott Joule (1818–1889); he did this by transferring accurately calibrated increments of mechanical energy to a known quantity of water (through viscous friction) and measuring the temperature increase; this established the so called *mechanical equivalent of heat*:

$$1 \text{ calorie} = 4.204 \text{ joules}$$

at 4°C. Heat capacities are typically given as *specific quantities*; a wide variety of units are used: joules/(meter³ · degree), ergs/(cm³ · degree), kilocalories/(mol · degree), etc. In modern experiments heat is applied electrically through a metal wire heater, the heat delivered being

$$Q(\text{joules}) = \text{voltage} \times \text{current} \times \text{time}.$$

Another question we might ask is what volume increment, ΔV , accompanies a temperature change ΔT ; this is governed by the *volume thermal expansion coefficient*

$\alpha \equiv \frac{1}{V} \frac{\partial V}{\partial T}$. Here again we can consider two cases

$$\alpha_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P ; \quad \alpha_S = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_S . \quad (4.53)$$

¹⁴ More precisely a calorie is the amount of heat needed to raise the temperature of water from 3.5 to 4.5 °C at standard atmospheric pressure; this interval is chosen since the density goes through a maxim at 4 °C and is therefore minimally sensitive to temperature changes. Conversions factors to other temperatures have been determined.

Note these quantities have been normalized so as to make them independent of the system volume, thereby making them “specific quantities” (see discussion in section 4.8).

A second quantity of interest is the compressibility, $\beta \equiv -\frac{1}{V} \frac{\partial V}{\partial P}$ (also written as χ) which governs the volume change, ΔV , accompanying a pressure change, ΔP applied to a system; we also introduce the bulk modulus, $B = -V \frac{\partial P}{\partial V}$. We have again normalized it relative to the volume to make it a specific quantity. Here the natural cases to consider are

$$\beta_T \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T ; \quad \beta_S \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S . \quad (4.53a,b)$$

and

$$B_T = -V \left(\frac{\partial P}{\partial V} \right)_T ; \quad B_S = -V \left(\frac{\partial P}{\partial V} \right)_S \quad (4.53c,d)$$

The relation between these quantities was determined earlier in Eq. (4.40). Note that we must have $\beta > 0$ if matter is to be stable; an increase in pressure always results in a smaller volume.

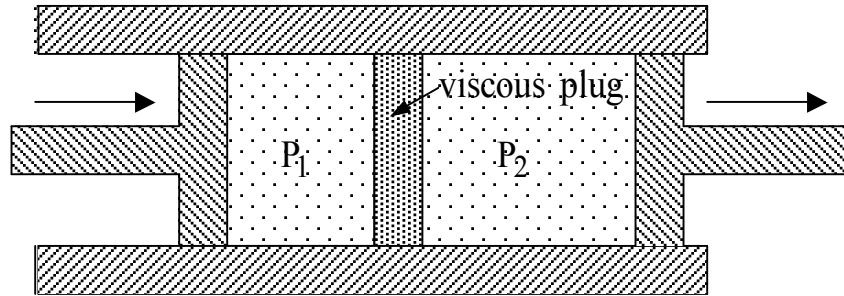


Fig. 4.2. The Joule-Thomson process, in which a gas is continuously passed from one chamber to another through a porous plug that produces a pressure difference $\Delta P = P_1 - P_2$ as the motion of the opposing pistons, creates a growing volume difference $\Delta V = V_1 - V_2$.

4.12 The Joule-Thomson process

Consider the process shown in Fig. 4.2 in which a gas is forced to flow through a “porous plug”¹⁵ in which the viscous drag on the gas flowing through it causes a drop in pressure from some input value P_1 to an output value P_2 . To maintain the pressures the pistons on each side of

¹⁵ One way to make such a plug is to tightly pack a non-conducting powder in a tube. The pressure drop arises from the flow resistance which is caused by the viscosity of the gas.

the apparatus are continually displaced. The energy change of the gas in passing through the medium is

$$\begin{aligned} E_1 - E_2 &= -\int dV_1 P_1 + \int dV_2 P_2 \\ &= -V_1 P_1 + V_2 P_2 \end{aligned}$$

where V_1 and V_2 are the volume changes resulting from the motion of the pistons. We rewrite this equation as

$$E_1 + V_1 P_1 = E_2 + V_2 P_2$$

or

$$W_1 = W_2; \quad (4.54)$$

i.e., the *enthalpy is conserved* in this process. Note entropy is not conserved since the viscous losses arising from the flow in the plug are irreversible.

For (4.54) to hold, generally, the temperature of the gas in the two chambers must differ¹⁶. A measure of this effect is then $(\partial T / \partial P)_W$ given by

$$\left(\frac{\partial T}{\partial P} \right)_W = \left(\frac{\partial(T, W)}{\partial(P, W)} \right) = \frac{\partial(T, W) / \partial(P, T)}{\partial(P, W) / \partial(P, T)} = - \frac{(\partial W / \partial P)_T}{(\partial W / \partial T)_P}.$$

From (14.21b) we recognize the denominator as C_P while the numerator follows from (4.23) as

$$\left(\frac{\partial W}{\partial P} \right)_T = T \left(\frac{\partial S}{\partial P} \right)_T + V = -T \left(\frac{\partial V}{\partial T} \right)_P + V,$$

where we used the Maxwell relation (4.22d) in the second step. Combining these two expressions we have

$$\left(\frac{\partial T}{\partial P} \right)_W = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T} \right)_P - V \right]. \quad (4.55)$$

Below some gas-specific temperature, called the Joule-Thomson inversion temperature, we may enter a regime where

$$T \left(\frac{\partial V}{\partial T} \right)_P < V$$

¹⁶ Eq.(4.54) then contains the additional assumption that there is no heat transfer between the two chambers. The plug must then be designed so that there is radial heat transfer (to disperse the viscous heating), but no axial heat transfer.

and the gas cools on passing through the plug; this is a commonly used refrigeration strategy.

As already remarked the entropy increases in the Joule-Thomson process. The first term for a small pressure differential is governed by $(\partial S / \partial P)_W$. To determine this quantity we rewrite the differential for the enthalpy, Eq. (4.23), as

$$dS = \frac{1}{T} dW - \frac{V}{T} dP,$$

from which it follows that

$$\left(\frac{\partial S}{\partial P} \right)_W = -\frac{V}{T}. \quad (4.56)$$

4.13. Relating work and entropy change in isolated bodies; extracting the maximum work

Suppose we have a *system* consisting of two *isolated bodies* that are separately in thermal equilibrium but that are not in equilibrium with each other. We can then ask: what is the *maximum* work that can be extracted in bringing them into equilibrium. In examining this question we will assume the bodies remain thermally isolated and that the total volume is the same at the beginning and end of the process (although it could change during the process)¹⁷. The bodies are then restricted to doing work on the environment, exchanging heat, or both.¹⁸. Any work performed by the system is assumed to be done on some *external object* and therefore energy, but not heat, is exchanged with that object, there being no direct thermal contact.

The work performed will be denoted as R . Now the convention in thermodynamics is that R is *less than* zero if work is done *by* the system. So when $R < 0$ the combined energy of the bodies changes from some initial value, E_0 , to some final value E where $E < E_0$. When equilibrium is achieved between the two bodies, by what ever processes we subject them to (including direct contact with each other but not with an external system), we can consider their *combined* energy as a function of their *combined* entropy, S ; i.e., $E = E(S)$. Since the system is thermally isolated, the total work performed by the system in coming into equilibrium then follows from conservation of the total energy as

$$|R| = E_0 - E(S); \quad (4.57)$$

¹⁷ In this way we exclude work done by expansion of the system as a whole, since such work could be done by a system in equilibrium.

¹⁸ A chamber containing some volume of compressed gas can always be expanded to do work.

here we wrote $|R|$ since the quantity on the right is positive, whereas R is negative as noted above (and zero when no work is extracted).

Suppose we differentiate (4.57) with respect to the final state entropy (recalling the total volume is assumed fixed) thereby forming the quantity

$$\frac{\partial |R|}{\partial S} = - \left(\frac{\partial E(S)}{\partial S} \right)_V ; \quad (4.58)$$

but

$$T = \left(\frac{\partial E(S)}{\partial S} \right)_V \quad (4.59)$$

so for small changes at constant volume we have

$$\delta |R| = -T \delta S . \quad (4.60)$$

Since the entropy of an isolated process can only increase (or at best remain constant), Eq. (4.60) tells us that when the volume is constant an increase in entropy implies a decrease in the amount of external work that can potentially be done by the system. Hence the system does the *maximum* external work if the entropy change is *minimal* (ideally zero); such processes are termed *reversible*. If we simply bring the two bodies into contact, heat will flow but *no* external work will be performed; such a process is then fully irreversible.

4.14. The Carnot cycle¹⁹

In the previous section we established that if we are to extract the maximum amount of work from two bodies at different temperatures we must do it in a reversible manner. In this section we describe a strategy for reversibly moving two bodies toward equilibrium in a step-like manner while simultaneously extracting the maximum amount of work. In doing this we will relax the requirement that no heat be conducted outside the bodies; instead small increments will

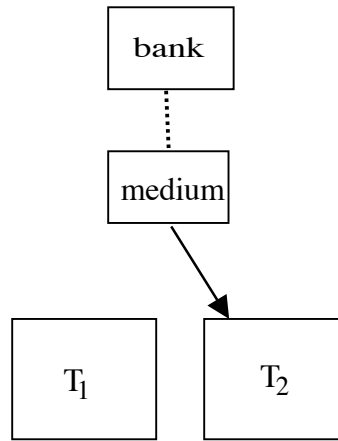


Fig. 4.3. Two bodies at temperatures T_1 and T_2 (with $T_2 > T_1$) which can alternately be connected to or isolated from a working medium that is in turn connected to an external body that serves as an energy bank from which the medium can make withdrawals and deposits and from which energy can be extracted for use outside the system.

¹⁹ Named for Nicolas Léonard Sadi Carnot, a French engineer.

alternately transferred from one body to a *working medium* which subsequently delivers it back to the second body (see figure 4.3). In doing this we must keep the temperature differentials, ΔT , small during the heat transfers since irreversible effects enter at the level of $(\Delta T)^2$. This is accomplished by having the medium undergo adiabatic processes in addition to isothermal ones.

The heat transfers and the work extracted are carried out with what is called a *Carnot engine* which consists of four steps and operates in a cyclic manner between our two *bodies* (also called *reservoirs*). To have a specific picture in mind we can take the medium to be a gas upon which work can be done (of either sign) by moving a piston. As already noted, only incremental quantities of work are to be performed with each cycle so as to keep the temperature change per cycle of the two bodies small, thereby maintaining near equilibrium conditions. Work increments performed during the steps are stored in an energy bank which we discuss further below. The four steps associated with the Carnot cycle are:

- 1) The medium, taken to be at a temperature $T_2 - \delta T$, is connected to body 2 having temperature T_2 and an increment of heat δQ_2 is transferred. To maintain an isothermal condition the gas is allowed to expand against the piston that confines it and the associated work performed, $|\delta R_2| = |P_2 \delta V|$, is deposited in the bank.
- 2) The medium and body 2 are disconnected after which the gas continues to expand, but now adiabatically, until the temperature falls to $T_1 + \delta T$ and the pressure to P_1 . The work performed by the piston displacement during this part of the cycle is also deposited in the bank.
- 3) The medium is now connected to body 1 at temperature T_1 and a heat δQ_1 is isothermally transferred to body 1 by compressing the gas and withdrawing an energy $|\delta R_1| = |P_1 \delta V|$ from the bank.
- 4) The medium is disconnected from body 1 and, through a further withdrawal from the bank, is adiabatically compressed to the point where the temperature returns to the initial value of $T_2 - \delta T$ and the pressure to P_2 , so that the cycle can be repeated.

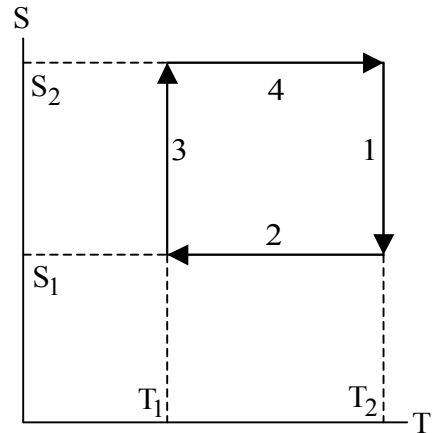


Fig. 4.4. The four steps in the Carnot cycle; the direction of the arrows corresponds to an engine which extracts work from the source at T_2 .

Note the work increments for the two adiabatic parts of the cycle will cancel each other; the net work performed arises from the two isothermal segments. The two isothermal (vertical arrows) and the two adiabatic

(horizontal arrows) parts of the cycle are shown in the entropy - temperature plane in Fig. 4.4 for the case where the cycle produces a net work. If we run the cycle in *reverse* there will be a net *withdrawal* of energy from the bank which is referred to as *refrigeration*.

The work increments can be used to accelerate (or decelerate depending on the sign) a rotating disc with a large moment of inertia (called a flywheel) that serves as the energy bank by storing kinetic energy. However use of a disc converts the *discrete* four-step cycle into an *oscillatory* one; this limits the time available to switch between the isothermal and adiabatic segments which results in some irreversibility. The combination of the working medium with its piston and the flywheel make up what can be called an *engine*. Energy can be extracted from the engine, via the shaft about which the flywheel rotates, and supplied to an external object called a *load*. This setup is shown in Fig. 4.5.

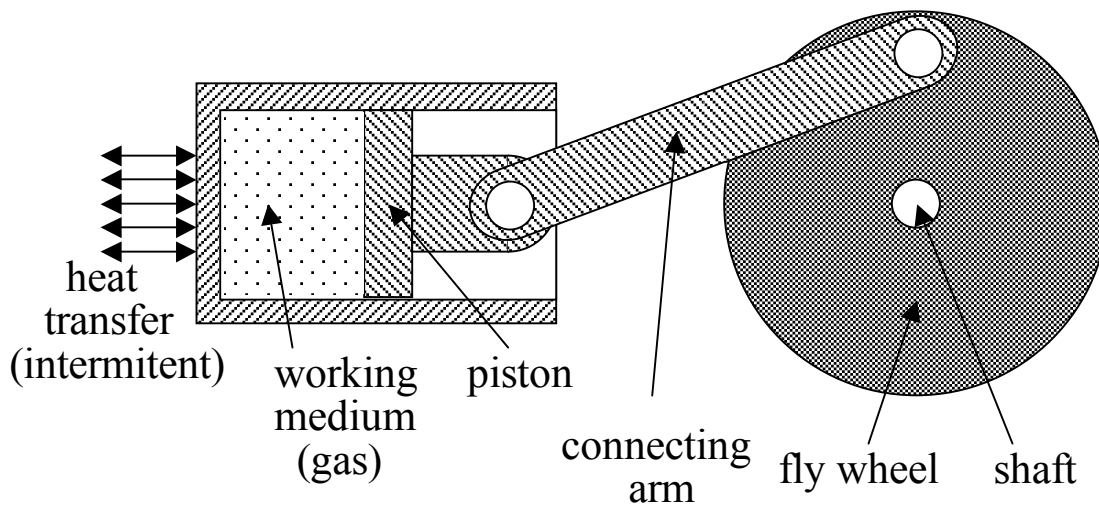


Fig. 4.5. A heat engine operating in four steps: 1) heat is introduced from a hot reservoir to expand the gas in the chamber and move the piston; 2) the chamber is disconnected from this reservoir and further expanded where it cools adiabatically to the temperature of a cold reservoir; 3) the chamber is connected to a cold reservoir and compressed as the heat generated is transferred to the cold reservoir; 4) the chamber is disconnected from the cold reservoir and further compressed raising its temperature to that of the hot reservoir.

We now examine the overall efficiency of the Carnot process. To avoid confusion with respect to signs we will take the absolute value of the relevant quantities. The energy taken from the (hotter) body 2 in step 1) of the cycle is

$$\begin{aligned} |\delta E_2| &= |dQ_2| = |T_2 \delta S_2| \\ &= |\delta R_2| \end{aligned} \tag{4.61a}$$

where in the second step we account for the work that the medium deposits in the bank. The corresponding energy delivered to the (colder) body 1 in step 3 is

$$\begin{aligned} |\delta E_1| &= |\delta Q_1| = |T_1 \delta S_1| \\ &= |\delta R_1| \end{aligned} \quad (4.61b)$$

where the second step accounts for the energy withdrawn from the bank. The overall work performed is then

$$\begin{aligned} |\delta R|_{\max} &= |\delta R_2| - |\delta R_1| \\ &= |\delta E_2| - |\delta E_1| = |T_2 \delta S_2| - |T_1 \delta S_1| \\ &= (T_2 - T_1) |\delta S_2| = \frac{T_2 - T_1}{T_2} |\delta E_2| \\ &= \eta |\delta E_2| \end{aligned} \quad (4.62)$$

where we assumed complete reversibility by writing $|\delta S_2| = |\delta S_1|$ in the third step. The quantity η introduced in the last step is called the *Carnot efficiency*; it measures how much energy can be extracted from a reservoir at one temperature (T_2) while discharging waste heat into a second reservoir at a lower temperature (T_1) while still conserving the overall energy. To turn *all* the internal energy into work (i.e., have $\eta = 1$) clearly requires $T_1 = 0$. If we allow T_2 to gradually approach T_1 (over many Carnot cycles) the system can be brought into equilibrium while simultaneously extracting the maximum overall work.²⁰

If the differential changes in Eq. (4.62) are performed in a time δt then our Carnot engine would deliver a *power* $|\delta R|_{\max} / \delta t$. To keep T_2 constant this would require heat input at a rate $\dot{Q} = |\delta E_2| / \delta t = \eta^{-1} |\delta R|_{\max} / \delta t$; to maintain steady conditions the same amount of heat must also be extracted from reservoir 1.

4.15. Work done by a body in contact with an external medium

We now examine possible behaviors a *small* object at temperature T and pressure P , which we will call the *body* that is coupled, thermally and/or mechanically, to a *much larger* object, here called the *medium*²¹, that is at some temperature and pressure, T_0 , P_0 (see Fig. 4.5.).

²⁰ To reversibly bring a system from one temperature to another while extracting no work requires a set of reservoirs at closely spaced intermediate temperatures. One then equilibrates the body at each temperature before proceeding to the next until the desired temperature interval is realized.

²¹ The term *bath* is also used in place of medium. Note our use of the term medium here is different from that in section 4.1.

We can think of the medium as a kind of *thermostat* that, due to its large size, maintains a constant temperature and pressure when changes occur in the body. We will also assume that the body can do work on an external object which we will call the *bank*; introducing the latter is a device (a trick) that allows the body to undergo reversible changes with respect to the medium. The body, bank, and medium are together taken to be an isolated system.

Now if the body is *isolated from* the medium any change in its energy can only go

into or out of the bank. However, in the presence of the medium, changes in the state of the system *depend on the path*; i.e., the nature of the coupling. We can then ask: what is the maximum work the body can do for a given change in its state when it is connected to, but not in equilibrium with, the medium? The connection to the medium allows the body to exchange heat with, and possibly do work on, the medium, *in addition* to any energy deposited in or withdrawn from the bank. If the body does work on the bank in changing its state, then in the reverse direction the bank does work on the body; i.e., *they have opposite signs*.

A finite increase in the *energy of the body* then consists of *three parts*: 1) the work done on the body by the bank; 2) the heat received from the medium; and 3) the work done on the body by the medium. Mathematically these three contributions are given by R , $-T_0\Delta S_0$, and $P_0\Delta V_0$ where the subscript zero denotes properties of the medium. Combining these we have

$$\Delta E = R - T_0\Delta S_0 + P_0\Delta V_0 . \quad (4.63)$$

We will take the *total volume* of the body and the medium to be a constant; then $\Delta V_0 = -\Delta V$. However the total entropy (body plus medium) can only increase; i.e., $\Delta S_0 + \Delta S > 0$ or $\Delta S_0 > -\Delta S$. Using these two results in succession Eq. (4.63) becomes

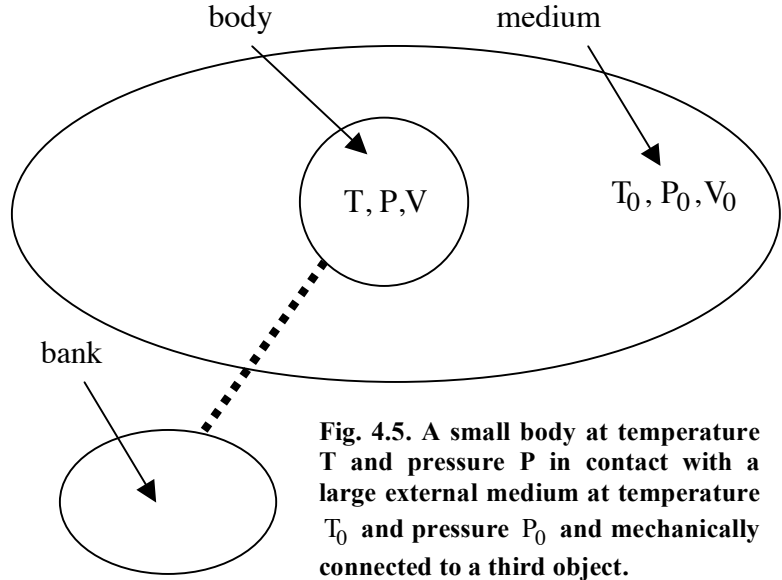


Fig. 4.5. A small body at temperature T and pressure P in contact with a large external medium at temperature T_0 and pressure P_0 and mechanically connected to a third object.

$$\begin{aligned}
R &= \Delta E + T_0 \Delta S_0 - P_0 \Delta V_0 \\
&= \Delta E + T_0 \Delta S_0 + P_0 \Delta V \\
&\geq \Delta E - T_0 \Delta S + P_0 \Delta V.
\end{aligned} \tag{4.64}$$

Equality in the last equation holds only for a *reversible* process and corresponds to the *minimum* work, R_{\min} , that the bank needs to perform to bring about the processes; i.e.,

$$R_{\min} = \Delta E - T_0 \Delta S + P_0 \Delta V. \tag{4.65}$$

4.16. Equilibrium and the Helmholtz and Gibbs free energies

Keeping in mind that P_0 and T_0 remain essentially constant (i.e., $\Delta P_0 \cong 0$; $\Delta T_0 \cong 0$), we may write (4.65) as

$$R_{\min} = \Delta(E - T_0 S + P_0 V). \tag{4.66}$$

On the other hand, the maximum work done in going the opposite direction (from the final state to the initial state) would be

$$|R|_{\max} = -\Delta(E - T_0 S + P_0 V). \tag{4.67}$$

Suppose the body passes through a series of states involving small changes in which it remains in equilibrium with itself (but not with the medium); we may then use the differential statement of the combined first and second laws, $dE = TdS - PdV$, and write (4.65) as

$$\begin{aligned}
dR_{\min} &= dE - T_0 dS + P_0 dV \\
&= TdS - PdV - T_0 dS + P_0 dV \\
&= (T - T_0)dS - (P - P_0)dV,
\end{aligned} \tag{4.68}$$

where we must again define a path if we are to integrate this expression.

We now consider two kinds of “contact” that our body might have with the medium such that it maintains the same temperature while undergoing some work R_{\min} , which is supplied by the bank. In the first process we assume the *volume of the body is held constant* ($\Delta V = 0$), say by having the body in a stiff box the walls of which conduct heat so that the temperature is constant and equal to that of the medium ($T = T_0$); however its entropy and energy are presumed to change as a result of some *internal* process involving additional degrees of freedom. Eq. (4.65) then gives

$$R_{\min} = \Delta(E - TS) = \Delta F; \tag{4.69}$$

the minimum required work is then equal to the change in the *Helmholtz* free energy, F .

For the second case we assume the body remains at the temperature and pressure of the medium (i.e., $P = P_0$; $T = T_0$) but that its volume, along with its energy and entropy, are now presumed to change²². Eq. (4.65) then gives

$$R_{\min} = \Delta(E + PV - TS) = \Delta G ; \quad (4.70)$$

the minimum required work is now given by the change in the *Gibbs* free energy.

Now suppose the body is in contact with the external medium (but not with a bank) and that it undergoes a *spontaneous* change in its state. Such changes can result from a chemical reaction (involving internal constituents), a transition from a metastable state, or a fluctuation²³. Since no work is done in such processes we set $R = 0$. If the temperature and pressure remain constant, i.e., $P = P_0$ and $T = T_0$, Eq. (4.64) takes the form

$$\Delta(E - T_0S + P_0V) \leq 0 , \quad (4.71)$$

from which we see that the Gibbs free energy must decrease and will only be a minimum when equilibrium is achieved. A similar statement holds for the Helmholtz energy for a process occurring at constant volume.²⁴

²² More generally, T and P may change during the process so long as they return to their original values at the end of the process.

²³ Fluctuations will be discussed in Chapter XX.

²⁴ In considering equilibrium in a thermodynamic system these conditions are typically just stated without proof; note their justification requires this somewhat complex argument.

Problems

- 4.1. Suppose an isolated gas in a volume V suddenly (irreversibly) expands by an amount dV , say by having one of the container walls instantaneously displace. The energy would be conserved in such a process and the resulting pressure change dP would be governed by the derivative $(\partial P / \partial V)_E$. Show this derivative is given by

$$\left(\frac{\partial T}{\partial V} \right)_E = \frac{1}{C_V} \left[P - T \left(\frac{\partial P}{\partial T} \right)_V \right].$$

- 4.2. Rather than the perfect gas law $PV = Nk_B T$, a gas of hard spheres, each with a volume b , can be approximately represented by the equation of state $P(V - Nb) = Nk_B T$. Calculate α_P and β_T for such a gas.

- 4.3. Calculate the relation between α_P and α_S (see Eq. (4.53)) for an arbitrary system in terms of readily measured quantities.

- 4.4. The so called van der Waals equation of state is given by

$$\left(P + \frac{N^2 a}{V^2} \right) (V - Nb) = Nk_B T.$$

There exists a temperature T_c , called the critical temperature, where the function $P = P(V, T)$ has an inflection point defined by the simultaneous conditions $(\partial P / \partial V)_T = 0$ and $(\partial^2 P / \partial V^2)_T = 0$. Find the accompanying pressure, $P = P_c$, and volume, $V = V_c$, at this point and compute the quantity $P_c V_c / Nk_B T_c$.

- 4.5. The so called Dietrici equation of state for a gas is given by

$$P(V - Nb) = Nk_B T \exp \left(- \frac{a}{Nk_B T V} \right).$$

As in the previous problem, find T_c , P_c , and V_c . Compute the quantity $P_c V_c / Nk_B T_c$ and compare it with the result found in the previous problem.

- 4.6. A van der Waals gas expands through a porous plug. Below some temperature the associated temperature change, which is governed by the derivative $(\partial T / \partial P)_W$ changes sign and the gas cools (this process is utilized in certain refrigerators). Calculate that temperature in terms of the parameters entering the van der Waals equation of state.