Thermal Physics Part 1

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Contents

1 Thermodynamic Systems

The *system* is the part of the universe in which we are interested (e.g. an object, a bulb of gas, a human being, the Earth, a galaxy etc). The surroundings (or thermal surroundings) are the rest of the universe. The universe is the systems plus the surroundings (Fig. 1.1).

Several systems of interest may be treated as a single *composite system* (Fig. 1.2). An *isolated system* is one that has no interaction (exchange of energy, matter, momentum, etc.) with other systems or the surroundings.
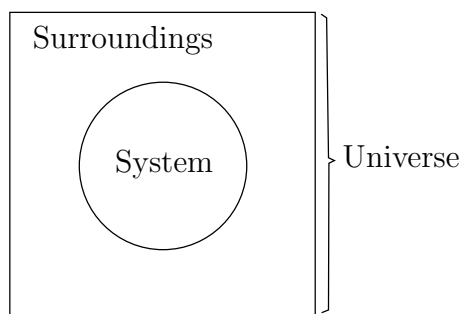
Figure 1.1
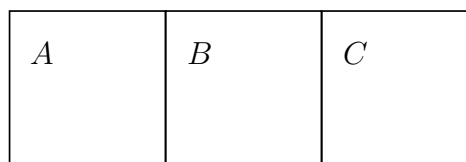
Figure 1.2

2 Equilibrium

Consider an isolated composite system containing gas (Fig. 2.1). No matter how complex the initial state, at long times the system will reach a state of *equilibrium* with time independent macroscopic properties (Fig. 2.2). Two types of property:

- *Intesive* - property of part of the system is equal to that of the whole system, e.g, p, T.

- *Extensive* - property of part of the system is different to that of the whole system, e.g, V, n.

Intensive properties are uniform/homogeneous at equilibrium. Thermodynamic variables are linked by equations of state:

$$p_A V_A = n_A R T_A; \ p_B T_B = n_B R T_B$$

Internal walls or constraint
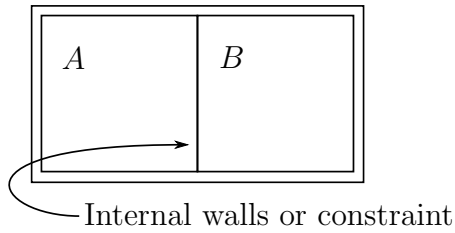
Figure 2.1

$$\begin{array}{|c|c|} \hline p_A & p_B \\ T_A & T_B \\ V_A & V_B \\ n_A & n_B \\ \hline \end{array}$$

Figure 2.2: Here p, T, V, n means pressure, temperature, volume, and number of moles, respectively

3   Thermal Contact

If A, B are in thermal contact then at equilibrium $T_A = T_B$ and A, B are said to be in *thermal equilibrium with each other*. Thermal contact is allowed by *diathermal walls* (Fig. 3.1) and prevented by *adiabatic walls* (Fig. 3.2). Diathermal walls allow the transfer of energy in the form of *heat* (thermal conduction, convection, radiation). Adiabatic walls forbid it. At thermal equilibrium all heat flow ceases.

If two systems (A, C) are in thermal equilibrium with a third (B) then they are in thermal equilibrium with each other. This is the *zeroth law* of thermodynamics which ensures temperature can be consistently defined. Temperature is the property that determines if systems are in thermal equilibrium with each other.

Diathermal walls

T_A T_B

$T_A = T_B$

Figure 3.1

Adiabatic wall

T_A T_B

$T_A \neq T_B$

Figure 3.2

A B C

$\left. \begin{array}{l} T_A = T_B \\ \\ T_B = T_C \end{array} \right\} \Rightarrow T_A = T_C$
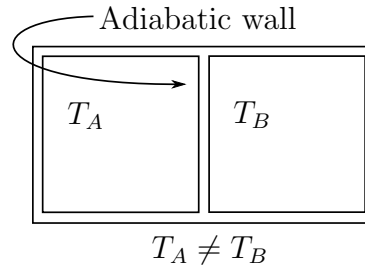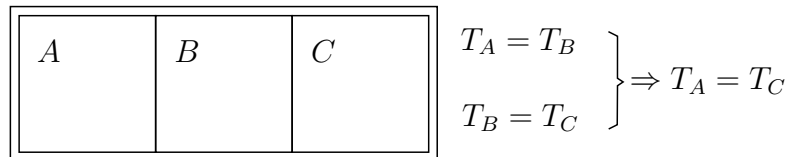
Figure 3.3

4   Mechanical Contact

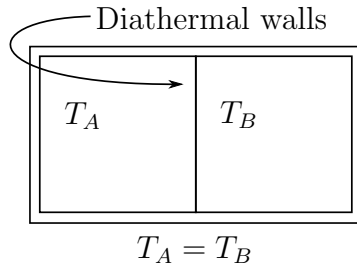If A, B are in *mechanical contact* then at equilibrium $p_A = p_B$ and A, B are said to be in *mechanical equilibrium* with each other. Mechanical equilibrium is allowed by *movable walls* (or flexible walls) and disallowed by *immovable walls* (or inflexible walls). Movable walls allow the transfer of energy in the form of *work* which is force times displacement. All forces are balanced at equilibrium ($p_A = p_B$).

Movable walls
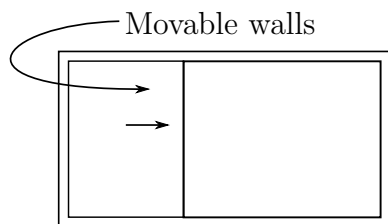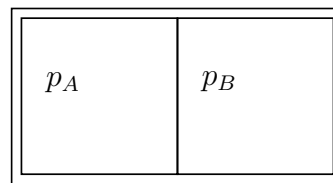
Figure 4.1

p_A p_B

$p_A = p_B$

Figure 4.2

5   Mass Contact

If A, B are in *mass contact* then mass can be exchanged between them, and they come to 'mass equilibrium'. A wall permeable to matter allows mass contact (Fig. 5.1); a wall impermeable to matter prevents it.

At mass equilibrium the gas densities ρ become equal (Fig. 5.2). Note that equilibrium (in these simple cases) involves homogeneity of intensive properties - T, p, ρ, etc.

Permeable walls

Figure 5.1

ρ_A ρ_B
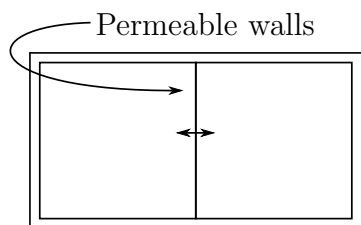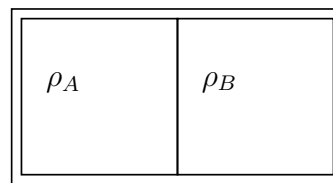
$\rho_A = \rho_B$

Figure 5.2

6   The Basic Problem of Thermodynamics

Many thermodynamic problems can be expressed in the following way:

What is the new equilibrium state reached after the removal of
internal constraints in an isolated composite system (Fig. 6.1)?

Later in the course we will give a completely general answer to this question.
But to start off with one will consider replacing an adiabatic wall with a diathermal
one so that heat can be exchanged.
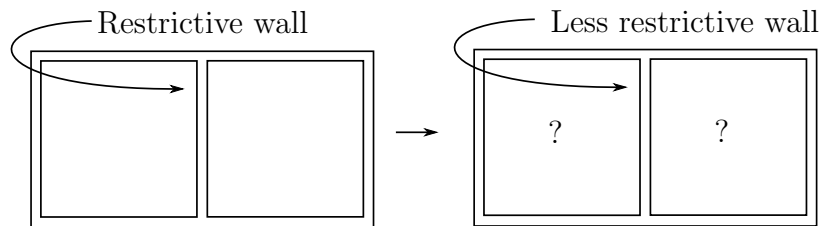
Figure 6.1

7 Heat Capacity C
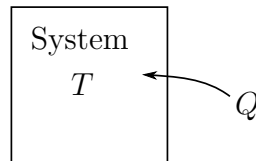
Figure 7.1: Energy added to the system in the form of heat (Q)

Say energy Q is added to the system in the form of heat (Fig. 7.1). The
temperature changes from T to $T + \Delta T$ and $\Delta T \propto Q$ so that $Q = C\Delta T$. As a
differential,

$$C = \lim_{\Delta T \to 0} \left(\frac{Q}{\Delta T} \right) = \frac{\text{đ}Q}{\text{d}T}$$

where the symbol đ will be explained later. Specific heat c is the heat capacity per
unit mass (or per unit mole, etc):

$$Q = mc\Delta T$$

Specific heats are only approximately temperature independent. For gases we must
specify them for constant pressure or volume.

8 The Final Temperature Problem

Object A at temperature T_A is placed in thermal contact with object B at temperature T_B. What is the final temperature (Fig. 8.1)?

We can formulate this in terms of the 'basic problem of thermodynamics'.

Solution: If $T_A > T_B$, heat flows from A to B:

$$\left.\begin{array}{c} Q_B > 0 \\ Q_A < 0 \end{array}\right) \quad \text{heat added to the system is positive:}$$

We have $Q_A = -Q_B$ by conservation of energy. So

$$C_A(T_f - T_A) = -C_B(T_f - T_B)$$

and thus

$$T_f = \frac{C_A T_A + C_B T_B}{C_A + C_B}$$

or equivalently

$$T_f = \frac{m_A c_A T_A + m_B c_B T_B}{m_A c_A + m_B c_B}$$

which is a kind of 'weighted averaged' and can be used to compare heat capacities.

Adiabatic wall   Diathermal wall

T_A T_B T_f T_f

Figure 8.1

9 Thermal Reservoir

Suppose

$$\frac{C_B}{C_A} = \frac{m_B c_B}{m_A c_A} = \quad \ll 1:$$

Then

$$T_f = \frac{T_A + T_B}{1 +}:$$
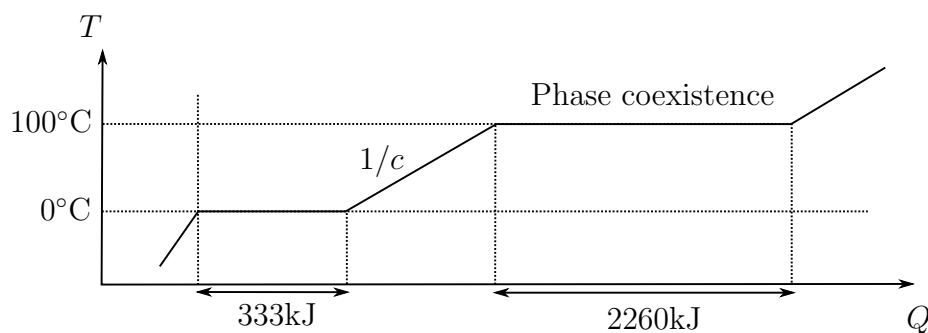
Figure 10.2

11 Thermal Conduction

Consider a rectangular parallelepiped (Fig. 11.1). We have

$$\frac{\text{d}Q}{\text{d}t} = -kA\frac{\text{d}T}{\text{d}t} = +kA\frac{T_{\text{hot}} - T_{\text{cold}}}{l}$$

at steady state. Here k is the *thermal conductivity* in $\text{Wm}^{-1}\text{K}^{-1}$. Suppose a hot source is a cooling object at temperature T, heat capacity C. Then

$$\text{d}Q = -C\,\text{d}T$$

$$\frac{\text{d}Q}{\text{d}t} = -C\frac{\text{d}T}{\text{d}t}.$$

So

$$\frac{\text{d}T}{\text{d}t} = -\frac{kA}{Cl}(T - T_{\text{cold}}).$$

Objects cool according to $e^{-\frac{kA}{Cl}t}$. The 'relaxation method' for comparing heat capacities or specific heats.

Figure 11.1

10
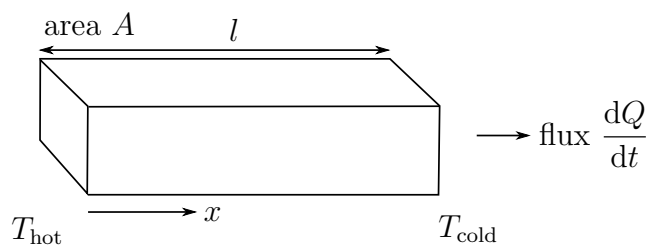
12 Joule's Paddle-Wheel Experiment (1843)

The work done by weight $w = mgh$ converted to heat in water $W = Q$, $Q = C\Delta T$ which implies

$$mgh = C\Delta T$$

This established the equivalence of heat and work. Doing work (mechanical or electrical) gives a third method of measuring heat capacity - but this time on an absolute scale.
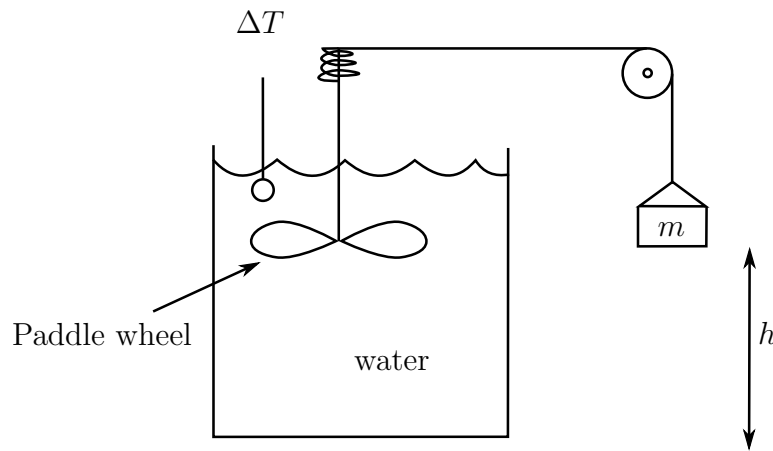
Figure 12.1

13 Interal Energy and the First Law

Processes Thermodynamics predicts that the result of a change between two equilibrium states A, B. The passage form A to B is called a *process*. A *quasistatic* process

Figure 13.2: Pushing weight along table: quasistatic, but irreversible
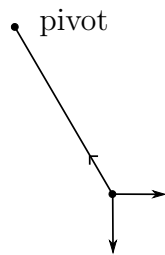
Figure 13.1: Slow raising of pendulum: quasistatic and (almost) reversible

involves a succession of equilibrium states. A *reversible* process is a quasistatic process in which no dissipative (e.g. frictional) forces act (Fig. 13.1). The opposite is an irreversible process (Fig. 13.2).

During a process, energy may be transferred between system and surroundings in different ways. We consider *heat* and *work*. A statement of energy conservation:

$$\Delta U = Q + W$$

This is the *first law of thermodynamics.* Here Q the is heat added to the system, W is the work done on the system, and ΔU is the change in the system's *interal energy.*

U is extensive and a function of the thermodynamic variables, called a *state function*:

$$U = U(p, T, n) = nu(p, T)$$
$$\text{or } nu(p, V)$$

where u is the internal energy per mole. For an ideal gas internal energy per mole depends on one independent variable– T:

$$u = u(T), \ U = nu(T)$$

Using differentials:
$$dU = đQ + đW.$$

Here đ denotes an inexact differential (Sect. 19).

14 pV **Work**
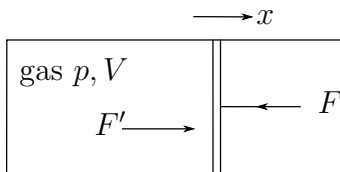
Figure 14.1

The set up is in Fig. 14.1. Assume the process is *quasistatic* so $F = F'$ at all points. Assume the process is *reversible* so all work goes into the gas (there is no

friction). Then

$$
\begin{aligned}
\text{d}W &= -F\,\text{d}x \\
&= -F'\,\text{d}x \\
&= -pA\,\text{d}x \\
&= -p\,\text{d}V\,.
\end{aligned}
$$

Note the sign on F acts to reduce V. Work is done on the gas when $\text{d}x < 0$ so $\text{d}W = 0$. Note we have expressed $\text{d}W$ in terms of the system properties p, V.

The expression works equally in expansion, so $\text{d}V > 0$ so $\text{d}W < 0$ – the gas does work. We can call this "pV" work. It applies to liquids and also solids under 'hydrostatic' pressure (equal from all sides) – not just gases.

15   Redefinition on Heat Capacity

The heat capacity C_V is at *constant volume*:

$$
C_V = \frac{\text{d}Q_V}{\text{d}T}
$$

where $\text{d}Q_V$ is the heat added at constant volume. The first law:

$$
\begin{aligned}
\text{d}U &= \text{d}Q + \text{d}W \\
&= \text{d}Q - p\,\text{d}V \\
&= \text{d}Q_V
\end{aligned}
$$

therefore

$$
\left(\frac{\partial U}{\partial T}\right)_V = \frac{\text{d}Q_V}{\text{d}T}.
$$

So

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

The heat capacity C_p is at *constant pressure*

$$
C_p = \frac{\text{d}Q_p}{\text{d}T}.
$$

The first law:

$$
\begin{aligned}
\text{d}U &= \text{d}Q + \text{d}W \\
&= \text{d}Q_p - p\,\text{d}V
\end{aligned}
$$

13

so
$$\text{d}Q_p = \text{d}U + p\,\text{d}V = c_p\,\text{d}T.$$

Now we can define the enthalpy
$$H = U + pV,$$

$$\text{d}H = \text{d}U + p\,\text{d}V + V\,\text{d}p.$$

At constant p: $\text{d}H = \text{d}U + p\,\text{d}V = C_p\,\text{d}T$. So
$$C_p = \left(\frac{\partial H}{\partial T}\right)_p.$$

H, like U, is a state function and extensive:
$$H = nh(p,V), U = nu(p,V).$$

Here h is the molar entropy.

16   The Case of an Ideal Gas

For an ideal gas $U = nu(T)$ so
$$C_V = n\left(\frac{\partial u}{\partial T}\right)_V = u\frac{\text{d}u}{\text{d}T}$$

therefore
$$\text{d}U = C_V\,\text{d}T =$$
$$= nc_V\,\text{d}T.$$

Consider the first law for a reversible change:
$$\text{d}U = \text{d}Q + \text{d}W$$
$$C_V\,\text{d}T = \text{d}Q - p\,\text{d}V$$

so
$$\text{d}Q = C_V\,\text{d}T + p\,\text{d}V$$

and
$$C_p = \frac{\text{d}Q_p}{\text{d}T} = C_V + p\left(\frac{\partial V}{\partial T}\right)_p. \tag{16.1}$$

14

Now, for an ideal gas, $pV = nRT$, so $V = nRT/p$ and

$$\left(\frac{\partial U}{\partial T}\right)_p = \frac{nR}{p}$$

From 16.1,

$$C_p = C_V + p\left(\frac{nR}{p}\right)$$

and so

$$C_p = C_V + nR$$

This is true for all gases at sufficiently low pressure. In fact, for a monatomic gas, $U = \frac{3}{2}nRT$ so

$$C_V = \frac{3}{2}nR, \ C_p = \frac{5}{2}nR \ \text{ (heat capacity)}$$

$$c_v = \frac{3}{2}R, \ c_p = \frac{5}{2}R \ \text{ (specific heat per mole)}$$

17 Temperature Dependence on U and H

The temperature dependence can be found by measuring C_V, C_p as a function of T (at fixed n).

$$C_V = \frac{\text{d}Q_V}{\text{d}T} = \left(\frac{\partial U}{\partial T}\right)_V$$

so

$$\int_{T_1}^{T_2} C_V \, \text{d}T = U(T_2) - U(T_1) = \Delta U$$

and

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

so

$$\int_{T_1}^{T_2} C_p \, \text{d}T = H(T_2) - H(T_1) = \Delta H.$$

Let $\Delta V = V(T_2) - V(T_1)$. Then $\Delta H = \Delta U + p\Delta V$. It is easier to fix pressure than volume, so measure ΔH and ΔV, then infer ΔU.

Both $H(T)$ and $U(T)$ increase with T, with 'jumps' at phase transitions (Fig 17.1). ΔV is finite at the transition. It is not possible to experimentally determine $U(T = 0)$ and $H(T = 0)$.

15
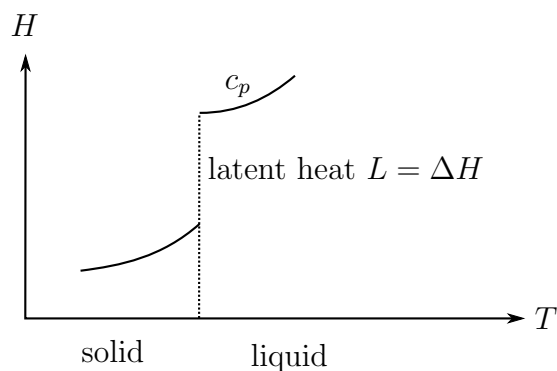
Figure 17.1

18   State Functions

At fixed n, $U = U(p, V)$. Changes in a *state function* like U depend only on the start and end points, not on the path or process:

$$\Delta U = U(p_B, V_B) - U(p_A, V_A).$$

But $\Delta U = Q + W$ and W *does* depend on the path, so $Q = \int \!\! dQ$ must also depend on the path (Fig. 18.1). Therefore Q and W *are not state functions.* We cannot write $Q(p, V)$ or $W(p, V)$. We can discuss "energy in a system" but not "heat or work in a system". Heat and work are forms of *energy transfer.*

Figure 18.1

16
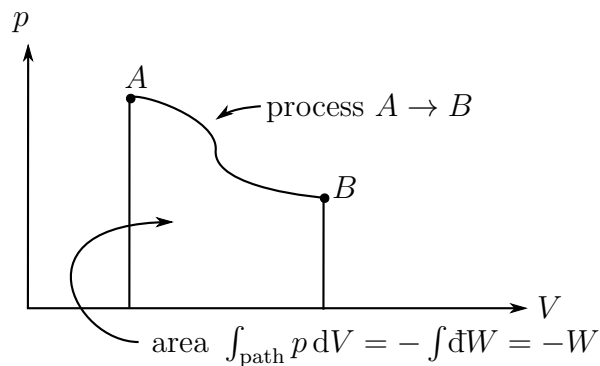
19　Notes

In mathematics if $f = f(x, y)$ (an 'explicit function' of x and y), then

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y\,.$$

Here $\mathrm{d}f$ is an "exact differential": $\int \mathrm{d}f$ is path-independent. Hence $\mathrm{d}U$ is an exact differential of $U(p, V)$. But $đQ$ and $đW$ are not. They are inexact differentials – hence the bar.

On (p, V) diagrams we will represent reversible processes as full lines and irreversible processes as dashed lines.
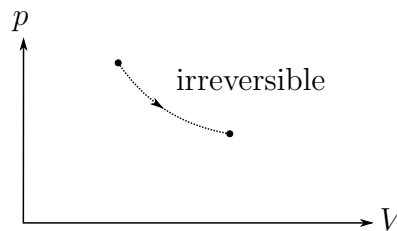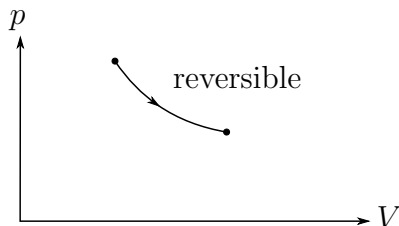
Figure 19.1: All states equilibrium states.

Figure 19.2: Only end points equilibrium states.

20　Thermodynamic Processes in an Ideal Gas

The *adiabatic free expansion* is irreversible because intermediate states are not equilibrium state (nonuniform density, pressure, etc). From the first law $\Delta U = Q + W$. The work W is zero as there is no opposing force and the heat Q is zero as the process is adiabatic. Thus $\Delta U = 0$. Since for an ideal gas $U = U(T)$, T is constant. From $pV = nRT$, pV is a constant. For example, V doubles and p halves.

21　Reversible Processes with a Fixed Parameter (constant n)

Types of processes:

- Isobaric - constant pressure

- Isovolumetric - constant volume

17

Adiabatic walls
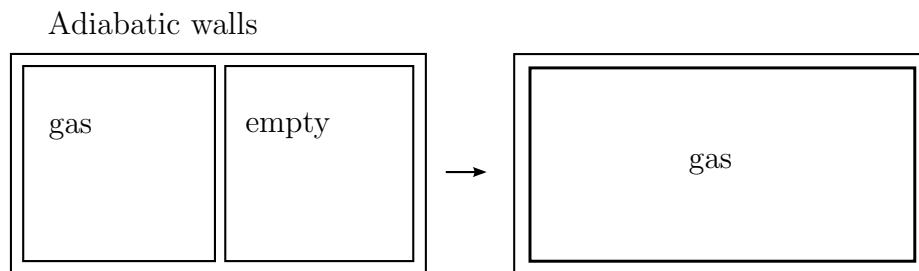
Figure 20.1

- Isothermal - constant temperature

The work W is

$$W = \int \mathrm{d}W = \int_{V_i}^{V_f} -p\,\mathrm{d}V$$

where V_i and V_f are the initial and final volumes, respectively. For an isobaric process:

$$W = -p \int_{V_i}^{V_f} \mathrm{d}V = -p(V_f - V_i).$$

Isovolumetric:

$$W = - \int p\,\mathrm{d}V = 0.$$

Isothermal:

$$W = - \int_{V_i}^{V_f} \frac{nRT}{V}\,\mathrm{d}V = -nRT \ln\left(\frac{V_f}{V_i}\right).$$

Since $U = \frac{3}{2}nRT = \frac{3}{2}pV$ for a monatomic ideal gas,

$$\Delta U = \frac{3}{2}(p_f V_f - p_i V_i).$$

We then use $\Delta U = Q + W$ to work out Q.

Isothermal case:

$$U = U(T), \text{ so } \Delta U = 0; \ Q + W = 0, \text{ so } Q = -W$$

and so

$$Q = +nRT \ln\left(\frac{V_f}{V_i}\right).$$

In an expansion the gas absorbs heat and converts it all to work. In a compression work is all converted to heat.

18

22 Reversible Adiabatic Expansion / Compression

Proof that pV^γ is a constant for an adiabatic expansion/compression, where $\gamma = C_p/C_V$. From the first law:

$$dU = \text{đ}Q + \text{đ}W,$$
$$dU = \text{đ}W \text{ (adiabatic)},$$
$$C_V\, dT = -p\, dV \text{ (ideal gas)},$$
$$C_V\, dT + p\, dV = 0 \text{ (reversible)}.$$

Since $pV = nRT$,

$$C_V + nRT\frac{dV}{V} = 0.$$

Dividing by T,

$$C_V\frac{dT}{T} + nR\frac{dV}{V} = 0.$$

As $C_p - C_V = nR$,

$$C_V\frac{dT}{T} + (C_p - C_V)\frac{dV}{V} = 0.$$

This becomes, by $\gamma = C_p/C_V$,

$$\frac{dT}{T} + (\gamma - 1)\frac{dV}{V} = 0$$

Integrating

$$\ln T + (\gamma - 1)\ln V = K''$$

so

$$TV^{\gamma-1} = K$$

where K is a constant. Using $T = pV/nR$,

$$\frac{p}{nR} \cdot V \cdot V^{\gamma-1} = pV^\gamma = K$$

for fixed n. For a monatomic ideal gas: $C_V = \frac{3}{2}nR, C_p = \frac{5}{2}nR$, so

$$\gamma = \frac{5}{3}$$

and so

$$pV^{5/3} = K.$$
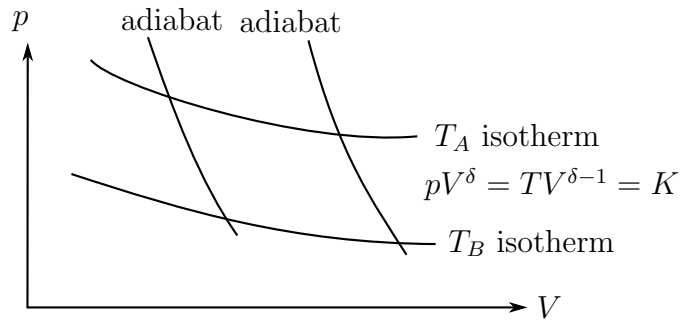
Figure 23.1

23 Interpretation

Adiabats are steeper than isotherms (Fig 23.1). The gas cools on adiabatic expansion and gas warms on aiabatic compression. Since $U = U(T)$ (increasing function), $\Delta U < 0$ for an expansion and by the first law $\Delta U = Q + W$ with $Q = 0$,

$$\Delta U = W \begin{cases} W < 0 & \text{for an expansion} \\ W > 0 & \text{for a compression.} \end{cases}$$

Therefore, for an adiabatic expansion ($W < 0$) internal energy is converted to work. For an adiabatic compression work is converted to internal energy.

24 Heat Engines and the Second Law
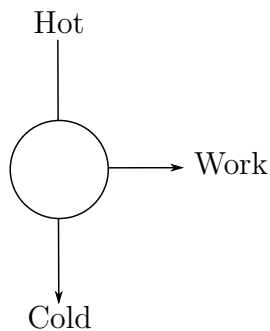
Figure 24.1

Heat flows from hot to cold. A heat engine (Fig 24.1) (or engine, steam engine, etc.) diverts some of this energy to do work. Note the non-standard sign convention in the figure. Question: how efficient can a heat engine be?
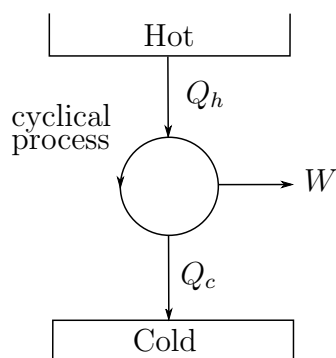
Figure 24.2: Q_h heat extracted from hot reservoir per cycle, Q_c heat delivered to reservoir per cycle, W work done per cycle
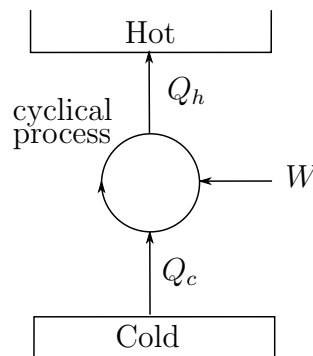
Figure 24.3

Carnot (1824) realised that the most efficient possible engine must be *reversible.* Otherwise friction diverts energy straight into the surroundings and misses an opportunity to do work. A *Carnot engine* is a *hypothetical* heat engine that (Fig. 24.2)

- has 2 thermal reservoirs (hot/cold)

- operates in a *cycle* with a *working substance*

- is reversible

An engine can be run in reverse to divert heat from cold to hot (Fig. 24.3)!

25   The Carnot Cycle

Consider a working substance which is an ideal gas with the cycle in Fig. 25.1.
   From the first law

$$\Delta U = 0 \text{ (cycle, state function)},$$

$$\Delta U = Q_h - Q_c - W.$$

Note the non-standard sign convention. Define the efficiency as

$$\eta = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h}$$

so that

$$\eta = 1 - \frac{Q_c}{Q_h}.$$
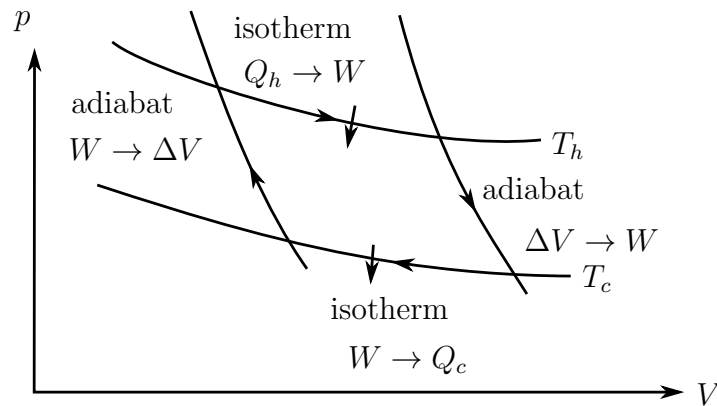
Figure 25.1

26 Carnot's Theorem
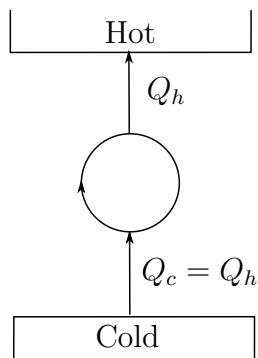
Figure 26.1
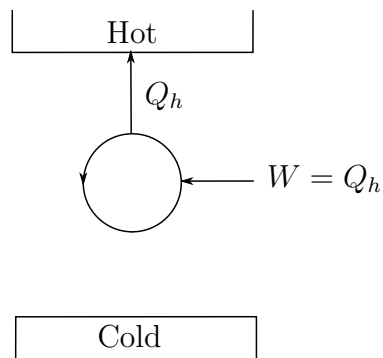
Figure 26.2

Historically this implied the second law. Here we postulate the second law and derive Carnot's theorem. Second law statements:

- Clausius: It is impossible to transfer heat spontaneously from cold to hot without causing other changes.

- Thomson (also known as Kelvin or Kelvin-Plank): A process whose only effect is the complete conversion of heat to work is impossible.

The application to cyclical processes is shown in Fig. 26.1 and Fig. 26.2. It can be shown the two statements are equivalent. Suppose we have two identical Carnot

engines, one driving the other in reverse (Fig. 26.3). The net effect is $|Q_h| = |Q'_h|$.
Now suppose that we have an engine that is more efficient than a Carnot engine (Fig.
26.4) it supplies the same work but extracts less heat Q''_h to do so. The net effect is
$Q_h - Q''_h > 0$ and $Q_c - Q''_c > 0$ which is in violation of the Clausius statement!

Carnot's theorem:

No engine operating between two thermal reservoirs can be more
efficient than a Carnot Engine operating between the same two reservoirs

Corollary: all Carnot (reversible) engines operating between (T_c, T_h) are equally
efficient.

There is a *fundamental limit* on the efficiency of heat engines that depends on
(T_c, T_h) and *not* on the details of engineering or the type of working substance:

$$\eta_{\max} = \eta_{\max}(T_c, T_h)$$

27   Kelvin's Absolute Thermodynamic Temperature

Since $\eta_{\max}(T_c, T_h) = 1 - Q_c/Q_h$, let us try defining temperature such that

$$\frac{T_c}{T_h} = \frac{Q_c}{Q_h}.$$

Then

$$\eta = 1 - \frac{T_c}{T_h}.$$

By considering the Carnot cycle for an ideal gas we can show that this definition is
consistent with the gas scale definition $T \overset{\text{gas}}{=} nR/pV$. But this definition of temperature
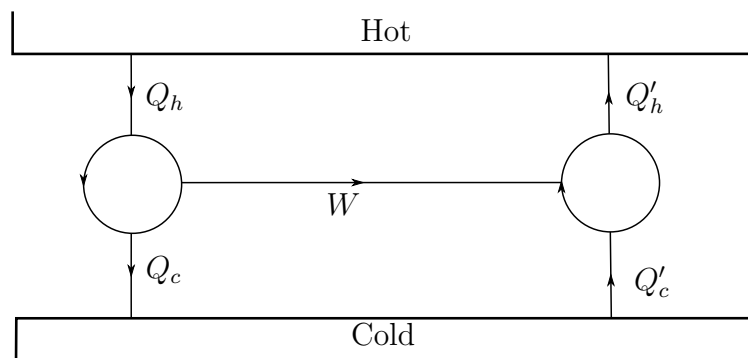
Figure 26.3
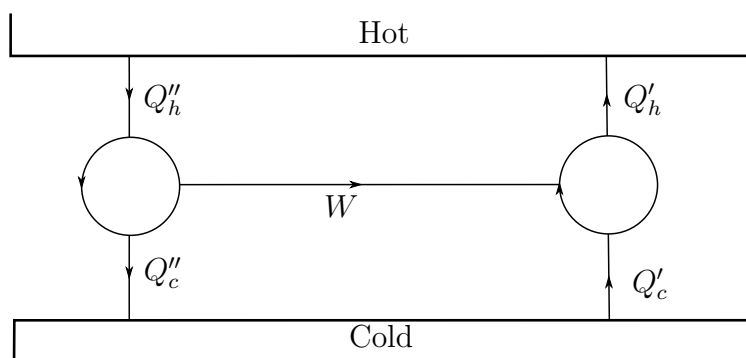
Figure 26.4
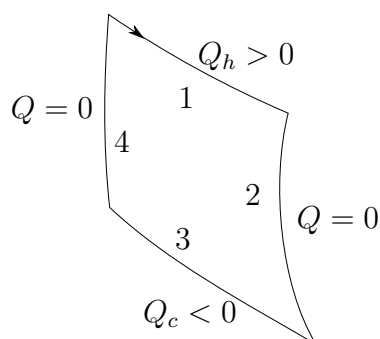
Figure 28.1
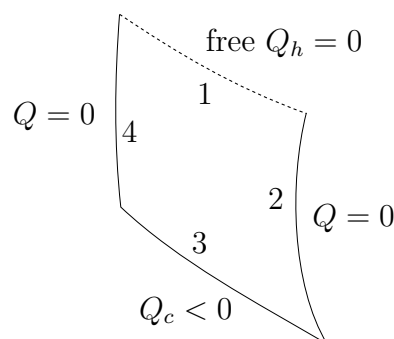
Figure 28.2

is independent of any particular substance or device (later we will find a definition that is independent of hypothetical engines as well).

28 Clausius Inequality

Consider two Carnot cycles (Fig. 19.1 and 28.2), one with the isothermal expansion replaced by an adiabatic free expansion (irreversible). Use conventional signs:

$$-\frac{Q_h}{Q_c} = \frac{T_h}{T_c}$$

and so

$$\frac{Q_h}{T_h} + \frac{Q_c}{T_h} = 0.$$

Therefore

$$\sum_i \frac{Q_i}{T_i} = 0.$$

Clausius argued that *any* cycle can be represented as the sum of Carnot cycles (Fig. 28.3). Making the sum an integral:

$$\oint \frac{\text{đ}Q}{T} \leq 0$$

which is the Clausius inequality for a system *doing* work. The equality applies to a *reversible* cycle.

29   Entropy

Now consider a reversible process (Fig. 29.1) ($\text{đ}Q_{\text{rev}}$)

$$\underbrace{\int_i^f \frac{\text{đ}Q_{\text{rev}}}{T}}_{\text{Path 1}} \text{I} + \underbrace{\int_f^i \frac{\text{đ}Q_{\text{rev}}}{T}}$$
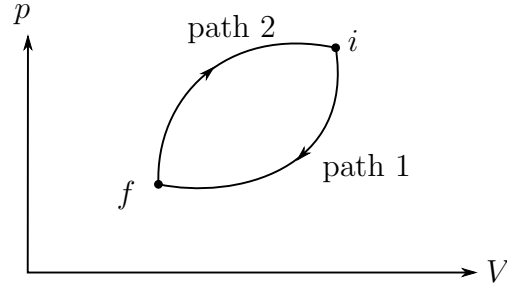
Figure 29.1

30 Law of Increase of Entropy

Compare a reversible change with a irreversible one (Fig. 30.1)

$$\oint \frac{\text{đ}Q}{T} \leq 0$$

implies

$$\int_i^f \frac{\text{đ}Q}{T} + \int_f^i \frac{\text{đ}Q_{\text{rev}}}{T} \leq 0$$

$$\int_i^t \frac{\text{đ}Q}{T} - \int_i^t \frac{\text{đ}Q_{\text{rev}}}{T} \leq 0.$$

Then

$$\Delta S = \int_i^t \frac{\text{đ}Q_{\text{rev}}}{T} \geq \int_i^f \frac{\text{đ}Q}{T}$$

For an infinitesimal process

$$\text{d}S \geq \frac{\text{đ}Q}{T} \text{ (equality denotes reversibility).}$$

For an isolated system $\text{đ}Q = 0$ and so

$$\text{d}S \geq 0.$$

This answer the 'basic problem' (Sect. 6). The final equilibrium state in an isolated system is that which maximises the entropy. Extending the isolated system to encompass the universe:

$$\text{d}S_{\text{universe}} \geq 0$$

for an real process (Clausius).
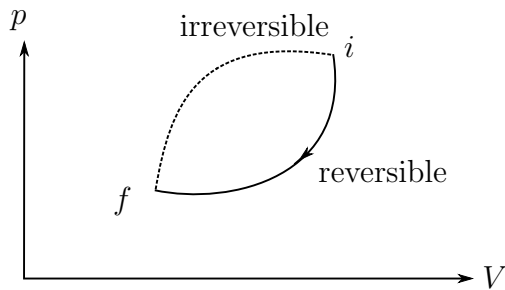
Figure 30.1

31 Equivalent Reversible Process

Previously we saw that a free expansion connects the same two equilibrium states as an isothermal expansion. Isothermal:

$$Q = nRT \ln \left(\frac{V_f}{V_I} \right)$$

and

$$\Delta S = \int \frac{\mathrm{d}Q_{\mathrm{rev}}}{T} = \frac{Q}{T} = nR \ln \frac{V_f}{V_i}.$$

Adiabatic free: $Q = 0$ and

$$\Delta S \geq \int \frac{\mathrm{d}Q}{T}$$

and so $\Delta S \geq 0$. This is all we can say, but since S is a state function, ΔS must be the same for the two processes. Hence for $\Delta S = nR \ln(V_f/V_i) \geq 0$.

Many *real* processes (all irreversible) have an equivalent reversible process from which we can calculate the entropy.

32 Statistical Interpretation of Entropy

Consider an adiabatic free expansion where one mole of an ideal gas doubles its volume (Fig. 32.1). Since $\Delta S = R \ln(V_f/V_i)$, $\Delta S = R \ln 2$. Boltzmann associated the entropy increase with a transition from a less probable to a more probable state (Fig. 32.2). To quantify, divide the box into $2m$ cells. Let Ω be the number of ways of arranging N atoms throughout the cells. $\Omega_1 = m^N$ (state 1); $\Omega_2 = m^{2N}$ (state 2). Let $S = k \ln \Omega$, so $\Delta S = k \ln(2m)^N - k \ln(m)^N = Nk \ln 2$. Then

$$\Delta S = R \ln 2$$

which is the same as above.

27
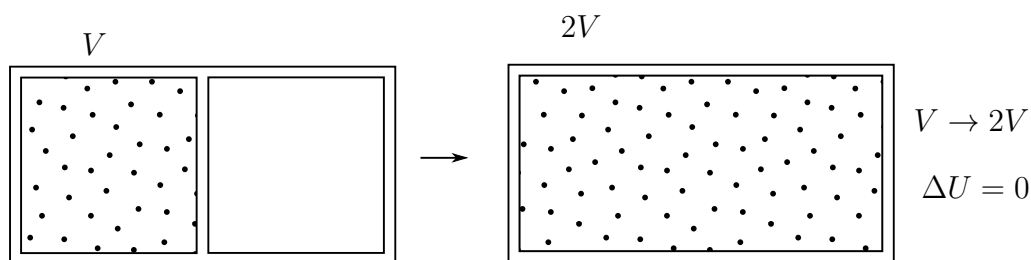
Figure 32.1

"Entropy is the number of ways of arranging the insides, such that the outside remain the same."

—Richard Feynmann
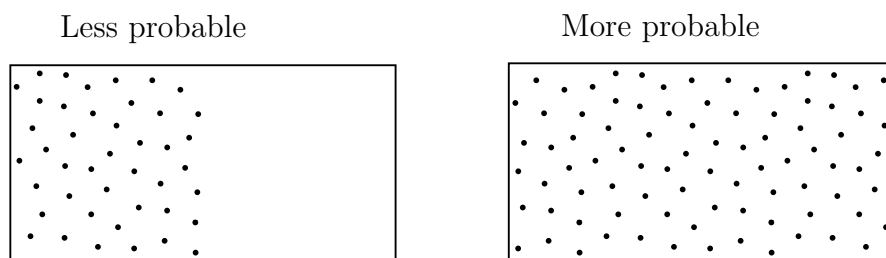
Figure 32.2

33   Temperature Dependence of Entropy at Fixed Pressure

Single phase:
$$\mathrm{d}S = \frac{\mathrm{d}Q_{\mathrm{rev}}}{T} = C_p \frac{\mathrm{d}T}{T}$$

At phase transition, $\Delta S = Q_{\mathrm{rev}}/T = L/T$ where L is the latent heat. In general:
$$\Delta S(T_i \to T_f) = \int_{T_i}^{T_f} \frac{C_p(T)}{T}\,\mathrm{d}T + \sum_{\text{phase changes}} \frac{L}{T}$$

Hence from $C_p(T)$ measurements $S(T)$ can be found (Fig. 32.3). There is experimental evidence that $S(T = 0) = 0$. Hence $S(T)$ can be put on an absolute scale (unlike $U(T)$ or $H(T)$). Also, S is extensive so we can define the *molar entropy* $s = S/n$. In general, $s(\text{gas}) > s(\text{liquid}) > s(\text{solid}) > s(\text{soft solid}) > s(\text{hard solid})$. E.g. for lead, $s = 15.5\mathrm{JK}^{-1}\mathrm{mol}^{-1}$ and for diamond $s = 0.6\mathrm{JK}^{-1}\mathrm{mol}^{-1}$.

28
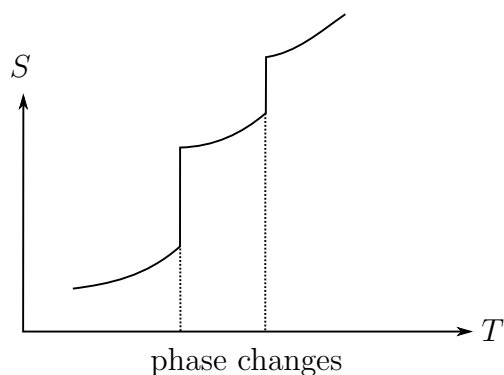
Figure 32.3

34 The Fundamental Equation

We can write the internal energy as a function of the extensive thermodynamic variables. For fixed n:

$$U = U(S,V)$$

and so

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \tag{34.1}$$

But from the first law:

$$dU = đQ + đW$$

and so

$$dU = T\,dS - p\,dV \tag{34.2}$$

which is the 'central equation' for reversible changes (i.e. $dS = đQ_{\text{rev}}/T$. Comparing 34.1 and 34.2, we see that

$$T = \left(\frac{\partial U}{\partial S}\right)_V ;\ p = -\left(\frac{\partial U}{\partial V}\right)_S$$

which is our final and best (?) definition of temperature. The fundamental equation can also be written

$$S = S(U,V).$$

All thermodynamic relations can be derived from this, but the actual form of the equation depends on the system. In practice 34.2 is more useful.

29

35 The Fundamental Equation for an Ideal Monatomic Gas

From the first law

$$\text{đ}Q = \text{d}U - \text{đ}W,$$
$$T\,\text{d}S = \text{d}U + p\,\text{d}V$$
$$\text{d}S = \frac{\text{d}U}{T} + \frac{p}{T}\,\text{d}V\,.$$

Using the equations of state $pV = nRT$, $U = \frac{3}{2}nRT$ and so

$$\text{d}S = \frac{3}{2}nR\frac{\text{d}U}{U} + nR\frac{\text{d}V}{V}.$$

Integrating we have

$$S = \frac{3}{2}nR\ln\left(\frac{U}{U_0}\right) + nR\ln\left(\frac{V}{V_0}\right) + S_0$$

where U_0, S_0, and V_0 define a reference state. This is the entropy fundamental equation for an ideal monatomic gas. Rearranging:

$$\frac{U}{U_0} = \left(\frac{V}{V_0}\right)^{-2/3} e^{(2/3nR)(S-S_0)}.$$

Application:

$$\left(\frac{\partial U}{\partial S}\right)_V = T = \left(\frac{2}{3nR}\right)U$$

and so

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

Also,

$$\left(\frac{\partial U}{\partial V}\right)_S = -p = \left(-\frac{2}{3V}\right)U$$

and so

$$p = \frac{nRT}{V}.$$

Now, instead of two equations of state, we have one single fundamental equation for the gas.

36   Helmholtz and Gibbs Free Energies

Consider a finite process in a system in contact with a thermal reservoir at temperature T. From second law, $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$. But as $T = T_{\text{surroundings}}$ is fixed the addition of heat to the surroundings is reversible:

$$\Delta S_{\text{surr}} = \int \frac{\text{đ}Q_{\text{rev}}}{T} = \frac{Q_{\text{surr}}}{T}.$$

With V fixed (no work), $\Delta U_{\text{sys}} = Q_{\text{sys}} = -Q_{\text{surr}}$ and so

$$\Delta S_{\text{surr}} = -\frac{\Delta U_{\text{sys}}}{T}.$$

Then

$$\Delta S_{\text{sys}} - \frac{\Delta U_{\text{sys}}}{T} \geq 0$$

or

$$\Delta[U_{\text{sys}} - T\Delta S_{\text{sys}}] \leq 0$$

for the system with constant T. Define $F = U - TS$ as the Helmholtz free energy and then $\Delta F \leq 0$. This is the system focused version of the second law for constrained T and V.

The case of fixed pressure:

$$\Delta H_{\text{sys}} = Q_{\text{sys}} = -Q_{\text{surr}}$$

and so

$$\Delta S_{\text{surr}} = -\frac{\Delta H}{T}.$$

Thus

$$\Delta[H - TS] \leq 0$$

for a system with T constrained. Define $G = H - TS$ and then $\Delta G \leq 0$. This is the Gibbs Free energy. It is the system focused version of the second law for fixed p and T.

We could also write

$$\begin{aligned}
\Delta G &= \Delta(U + pV - TS) \\
&= \Delta U + p\Delta V - T\Delta S \\
&= \Delta F + p\Delta V \\
&= \Delta F + W
\end{aligned}$$

and so $\Delta G \leq 0$ implies $\Delta F + W \leq 0$ or

$$W \leq -\Delta F.$$

The maximum work available from a process (at constant T) is $-\Delta F$, not $-\Delta U$. Hence the name "free" energy – the energy available to do work.

37   Natural Variables

In $W = -p \, dV$ we have to express p as a function of V to integrate. Similarly, in $dU = T \, dS - p \, dV$, S and V are 'natural variables' but usually we would prefer (V, T) or (p, T).

Start with $dU = T \, dS - p \, dV$, and substitute:

$$F = U - TS,$$

$$dF = dU - T \, dS - S \, dT$$

and so

$$dF = -S \, dT - p \, dV$$

so T and V are the natural variables. For the Gibbs free energy

$$G = H - TS = U + pV - TS,$$

$$dG = dU + p \, dV + V \, dp - T \, dS - S \, dT$$

and so

$$dG = V \, dp - S \, dT$$

and here p and T are the natural variables.

These are useful equations when we required natural variables V, T and p, T, respectively.

Transformations like

$$F = U - TS, \ G = H - TS, \ H = U + pV$$

are called *Legendre Transforms*.

38 Maxwell Relations

If we have an exact differential of $f(x, y)$

$$\mathrm{d}f = \left(\frac{\partial f}{\partial x}\right)_y \mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)_x \mathrm{d}y = A\,\mathrm{d}x + B\,\mathrm{d}y$$

then it follows that

$$\left(\frac{\partial A}{\partial y}\right)_x = \left(\frac{\partial B}{\partial x}\right)_y.$$

Let's choose one of the above relations, e.g. $\mathrm{d}F = -p\,\mathrm{d}V - S\,\mathrm{d}T$,

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

which is a "Maxwell Relation". It is completely general – it applies to all systems. In an experiment if we want to know how entropy changes with volume, we could get it by measuring $(\partial p/\partial T)_V$.

39 Thermodynamics – A Final Word

Thermodynamics boils down to just two equations:

$$\mathrm{d}U = đQ + đW,$$

$$\mathrm{d}S \geq \frac{đQ}{T}.$$

For reversible (or equivalent reversible) processes we can write $\mathrm{d}S = đQ_{\mathrm{rev}}/T$ and derive (at fixed n):

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V.$$

To be clear - this equation is true for all changes between equilibrium states, not just reversible ones, because it follows from $U = U(S, V)$.

Using Legendre transforms like $H = U + pV$, $F = U - TS$, $G = H - TS$, we can derive equations like

$$\mathrm{d}F = -p\,\mathrm{d}V - S\,\mathrm{d}T$$

etc. From these, we can get other usual equations. Finally, note the similarity between $đQ_{\mathrm{rev}} = T\,\mathrm{d}S$ and $đW = -p\,\mathrm{d}V$. Just as pressure is the thermodynamic variable conjugate to volume, so temperature is the thermodynamic conjugate to entropy.

40 Kinetic Theory

From thermodynamics, the details of any system are inserted by specifying either the form of the 'fundamental equation' or (equivalently) two equations of state. For example, for an ideal gas (monatomic)

$$pV = nRT, \; U = \frac{3}{2}nRT.$$

Let's write these in the form of a 'mechanical' equation

$$pV = \frac{2}{3}U$$

and a 'thermal' equation

$$U = \frac{3}{2}nRT$$

and try to derive these from a microscopic theory of gas 'molecules' (strictly atoms in this case).
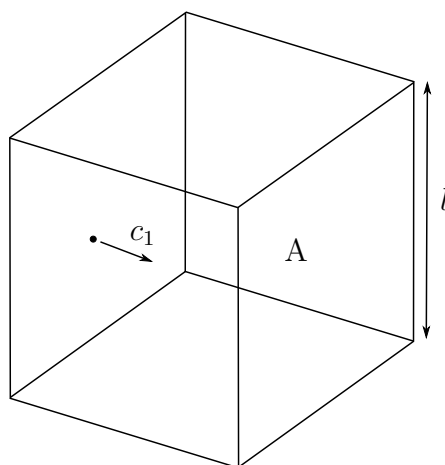

Figure 40.1

41 'Heuristic' Argument for Gas Pressure

Assume that:

- The molecules are elastic point masses,

- There are negligible intermolecular interactions,

- The time of collision is negligible compared to time between collisions.

A cube with N molecules of mass m. Molecule 1, speed c, moves towards face A (Fig. 40.1). The momentum change on impact is is $mc - (-mc) = 2mc$. The number of impacts per second is c/l. The momentum change per second is $2mc^2/l$ which is the force. On average, $N/6$ molecules maintain pressure on face A. The average force

$$\bar{F} = \frac{N}{6} \frac{2m \langle c^2 \rangle}{l} = \frac{1}{3} \frac{Nm \langle c^2 \rangle}{l}$$

so

$$p = F/A = \frac{1}{3} \frac{nm \langle c^2 \rangle}{l^3} = \frac{1}{3} \frac{nm \langle c^2 \rangle}{V}.$$

Finally

$$pV = \frac{1}{3} nm \langle c^2 \rangle.$$

But U is the total energy which is N times the average kinetic energy per molecule. So

$$U = \frac{1}{2} nm \langle c^2 \rangle$$

or

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

We have derived $pV = \frac{2}{3}U$, but not $U = \frac{3}{2}NkT$. However, if we accept $U = \frac{3}{2}NkT$ then it follows $\frac{1}{2}Nm \langle c^2 \rangle = \frac{3}{2}NkT$ and so

$$\langle E \rangle = \frac{3}{2} kT$$

where $\langle E \rangle$ is the average kinetic energy per molecule. We have

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT$$

or

$$\frac{1}{2} m \langle v_x^2 + v_y^2 + v_z^2 \rangle = \frac{3}{2} kT.$$

Now because gas is *isotropic*

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{kT}{m}$$

and
$$\langle E_x \rangle = \langle E_y \rangle = \langle E_z \rangle = \frac{1}{2}kT$$

where $E_x = \frac{1}{2}mv_x^2$ etc.

To calculate averages we need a probability distribution. Here we give a simple argument for the Boltzmann distribution, based on $S = k\ln\Omega$. Imagine N atoms, each with 2 energy levels $E = 0$ and $E = \varepsilon$. With n exited atoms $U = n\varepsilon$. Hence the probability an atom is excited is $P(E = \varepsilon) = n/N$. Now, excite one extra atom, n becomes $n + 1$ and

$$\Omega_{\text{before}} = \frac{N!}{n!(N-n)!}; \quad \Omega_{\text{after}} = \frac{N!}{(n+1)!(N-n-1)!}$$

so

$$\frac{\Omega_{\text{after}}}{\Omega_{\text{before}}} = \frac{N-n}{n+1} \approx \frac{N-n}{n} = \frac{N}{n} - 1$$

if $n \gg 1$. So

$$\Delta S = k\ln\Omega_{\text{after}} - k\ln\Omega_{\text{before}} = k\ln\left(\frac{N}{n} - 1\right).$$

Thus, as $\Delta U = \epsilon$,

$$T = \frac{\Delta U}{\Delta S} = \frac{\varepsilon}{k\ln(N/n - 1)}$$

so that

$$\frac{N}{n} - 1 = e^{\varepsilon/kT}$$

and

$$\frac{n}{N} = \frac{1}{1 + e^{\varepsilon/kT}} = \frac{e^{-\varepsilon/kT}}{1 + e^{-\varepsilon/kT}} = \frac{e^{E_1/kT}}{\sum_i e^{-E_i/kT}}$$

where $E_0 = 0, E_1 = \varepsilon$. Thus

$$\frac{n}{N} = P(E = E_i) = \frac{e^{-E_i/kT}}{\displaystyle\sum_{i=0,1} e^{-E_i/kT}}.$$

It can be shown that this relation is general:

$$P(E = E_i) = \frac{e^{-E_i/kT}}{\sum_j e^{-E_j/kT}}.$$

This is the Boltzmann distribution for the probability of occupation of the ith level out of a set of j levels. More simply

$$P_i \propto e^{-E_i/kT}$$

or

$$P_i = C(T)e^{-E_i/kT}$$

where $C(T)$ is a constant that normalises the distribution.

Armed with the Boltzmann distribution, we will go on to prove our second equation of state

$$U = \frac{3}{2}nRT$$

Figure 41.1

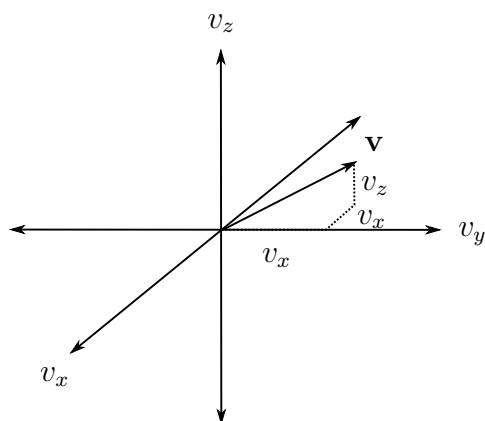## 42   Molecular Velocity Distribution

Write the velocity of a gas 'molecule' (here an atom) as

$$\mathbf{v} = (v_x, v_y, v_z)$$

Represent the possible velocities on an graph (Fig. 41.1).

The energy of a state $E(v_x, v_y, v_z) = \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$. The probability of occupying a state (Boltzmann):

$$P(v_x, v_y, v_z) \propto e^{-(1/2)m(v_x^2+v_y^2+v_z^2)/kT}$$

37

$$P(v_x, v_y, v_z) = ce^{-(1/2)m(v_x^2+v_y^2+v_z^2)/kT}$$

The constant c can be found by 'normalising' the distribution (density function), such that the integral over all 'velocity space' is unity:

$$\int_{\text{all space}} p(v_x, v_y, v_z)\, \mathrm{d}v_x\, \mathrm{d}v_y\, \mathrm{d}v_z = 1$$

so that

$$c = \left(\frac{m}{2\pi kT}\right)^{3/2}$$

The physical interpretation is $p(v_x, v_y, v_z)\, \mathrm{d}v_x\, \mathrm{d}v_y\, \mathrm{d}v_z$ proportionla to the number of molecules with velocities in the range (v_x, v_y, v_z) to $(v_x + \mathrm{d}v_x, v_y + \mathrm{d}v_y, v_z + \mathrm{d}v_z)$. This is the "Maxwell-Boltzmann distribution of molecular velocities" (Fig. 42.1).
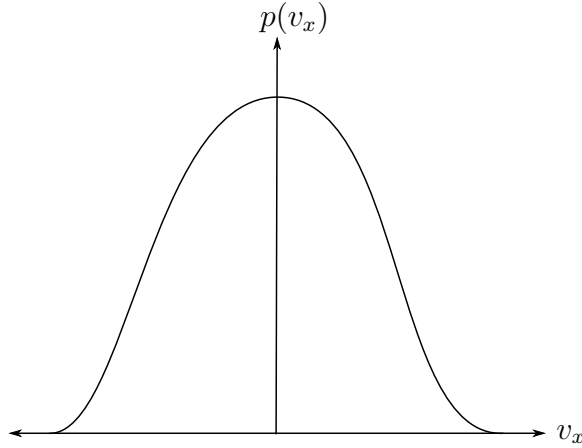
Figure 42.1: Gaussian or normal curve.

43   Molecular Speeds Distribution

This speed is $s = |\mathbf{v}| = |(v_x, v_y, v_z)| = \sqrt{v_x^2 + v_y^2 + v_z^2}$. Since $p(v_x, v_y, v_z) \propto e^{-\frac{1}{2}m(v_x^2+v_y^2+v_z^2)/kT}$, we *could* write $p(s) \propto e^{-\frac{1}{2}ms^2/kT}$, *but* this does not recognise that many different velocities share the same speed (Fig. 43.1). It follows that $p(s) \propto s^2 e^{-\frac{1}{2}s^2/kT} = c's^2 e^{-\frac{1}{2}ms^2/kT}$. Normalising:

$$\int_0^\infty c's^2 e^{-\frac{1}{2}ms^2/kT} = 1$$

38

45 The Energy Distribution

Is the energy distributed as broadly as the speed?

$$E = \frac{1}{2}ms^2; \quad \frac{\mathrm{d}s}{\mathrm{d}E} = \frac{1}{\sqrt{2mE}}; \quad s^2 = 2E/m$$

and so

$$P(E) = p(s)\left|\frac{\mathrm{d}E}{\mathrm{d}s}\right|^{-1} = c'\left(\frac{2E}{m}\right)\frac{1}{\sqrt{2mE}}e^{-E/kT}.$$

Thus

$$P(E) = c'E^{1/2}e^{-E/kT}.$$

This is for *one* molecule, it is a broad distribution, but $U = E_1 + E_2 + E_3 \ldots + E_n$. For N molecules, the curve sharpens with respect to its most probable value, a consequence of the *central limit theorem* of statistics (Fig. 45.1). In fact, the 'width' ΔU is given by $\Delta U/\langle U\rangle \sim 1/\sqrt{N}$.
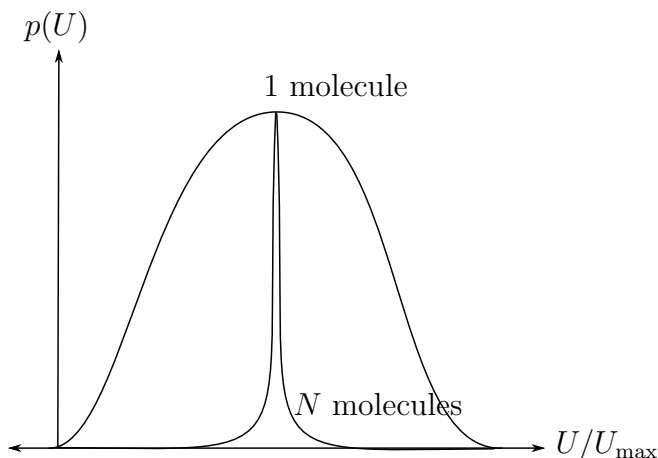
Figure 45.1

Here U is effectively not distributed, and we wirte it as U and not $\langle U\rangle$, as in thermodynamics. The large N limit is hence called the 'thermodynamic limit'.

46 Equipartition Principle

By integrating the speeds distribution we showed that the average kinetic energy of a molecule is $\frac{3}{2}kT$. If we write

$$\langle E\rangle = \frac{1}{2}m\left\langle v_x^2 + v_y^2 + v_z^2\right\rangle$$

40

then

$$\langle E_x \rangle = \frac{1}{2} m \langle v_x^2 \rangle = \frac{1}{2} kT,$$

$$\langle E_y \rangle = \frac{1}{2} m \langle v_y^2 \rangle = \frac{1}{2} kT,$$

$$\langle E_z \rangle = \frac{1}{2} m \langle v_z^2 \rangle = \frac{1}{2} kT,$$

found directly by integrating the velocity distribution.

Suppose we had a Hooke's law $E = \frac{1}{2} kx^2$ where k is the force constant and x is the displacement. Assuming the 'states' are uniformly distributed in coordinate x, the maths is the same but with different symbols!

$$\langle E_{\text{Hooke}} \rangle = \frac{1}{2} kT$$

Each "squared term" of a velocity (momentum) or coordinate in the energy contributes $\frac{1}{2} kT$ to the average energy. This is called the *classical equipartition.*

47   Degrees of Freedom

Consider a molecule of M atoms. The number of degrees of freedom (d.o.f.) is the number of coordinates needed to describe the positions of all the particles, i.e. $(x, y, z) \times M = 3M$.

- The centre of mass needs three coordinates, so there are three translational d.o.f.

- For a linear molecule, rotation requires two angles (θ, ϕ) angles, so three rotational d.o.f.

- For a nonlinear molecule, rotation requires one more angle, so three rotational d.o.f.

- The remainder of the $3M$ d.o.f. is accounted for by vibrations.

48   Application to Molecular Energies

The motion of molecules can be seperated into three components:

- Translations

- Rotations

- Vibrations

Each contributes "squared terms" to the energy.

- Translations: Three d.o.f.,

  Three squared terms ($\frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$,

  $\langle E_{\text{trans}} \rangle = \frac{3}{2}kT$.

- Rotations: One squared term per rotational d.o.f., e.g. $E = \frac{1}{2}I\omega^2$,

  $\langle E_{\text{rot}} \rangle = \frac{1}{2}kT$ per rotational d.o.f.

- Vibrations: Two squared terms (i.e. potential energy, kinetic energy),

  $\langle E_{\text{vib}} \rangle = kT$ per vibrational d.o.f.

49   Recipe for Calculating Energy

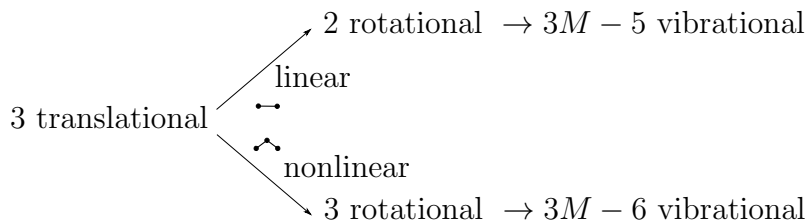M atoms in a molecule, so there are $3M$ d.o.f.. (Fig. 49.1).

2 rotational $\rightarrow 3M - 5$ vibrational

linear

3 translational

nonlinear

3 rotational $\rightarrow 3M - 6$ vibrational

Figure 49.1

	Linear	Nonlinear
Translational	$3/2kT$	$(3/2)kT$
Rotational	kT	$(3/2)kT$
Vibrational	$(3m-5)kT$	$(3m-6)kT$

Example of water vapour. We have $M = 3$ so 9 d.o.f.We have

$$\langle E_{\text{trans}} \rangle = \frac{3}{2}kT, \ U_{\text{trans}} = \frac{3}{2}nRT$$

$$\langle E_{\text{rot}} \rangle = \frac{3}{2}kT, \ U_{\text{rot}} = \frac{3}{2}nRT$$

$$\langle E_{\text{vib}} \rangle = 3kT, \ U_{\text{vib}} = 3nRT,$$

So that $U = 6nRT$. Also, $C_V^{\text{trans}} = \frac{3}{2}nR$, $C_V^{\text{rot}} = \frac{3}{2}nR$, $C_V^{\text{vib}} = 3nR$. An experiment is shown in Fig. 49.2.
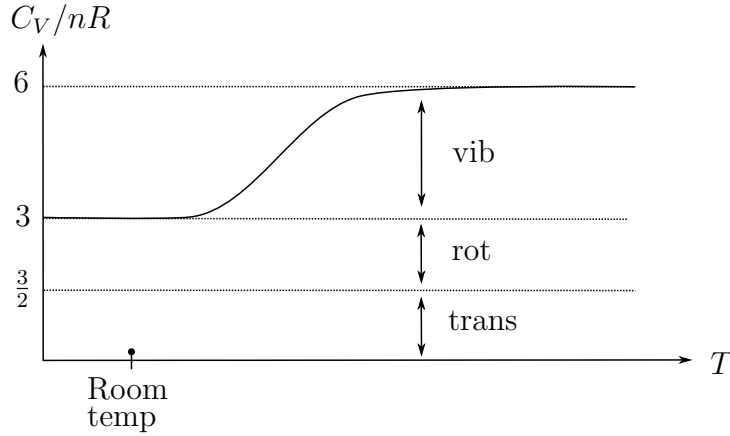

Figure 49.2

The vibrational d.o.f. are *dormant* at room temperature. This is *not* in classical physics! Errors comes from approximating discrete energy levels as a continuous spectrum.

According to $P_i \propto e^{-E_i/kT}$, level will accept *no energy* if $kT \ll E_i$.

50 Discussion

Such breakdowns of classical equipartition were discovered in specific heats of gases, crystals ('Dulong-Petit Law') and thermal radiation (Planck spectrum). It contributed to the birth of quantum mechanics.

In quantum mechanics, the more 'confined' a motion, the larger its 'quantum' (energy-level spacing) and the higher a temperature is required to 'turn on' the specific heat.

Specific heat of internal motions of an atom (electronic, nuclear) is measurable only at $T \gg 300$K. The complexity of $U(T)$ for the 'average' molecule explains why physicists were so slow to embrace the chemists' atomic model.

Final note:
$$\langle \text{kinetic energy} \rangle \propto T$$

is *only* true of an ideal gas- not general!