

Section 3

Entropy and Classical Thermodynamics

3.1 Entropy in thermodynamics and statistical mechanics

3.1.1 The Second Law of Thermodynamics

There are various statements of the second law of thermodynamics. These must obviously be logically equivalent. In the spirit of our approach we shall adopt the following statement:

- *There exists an extensive function of state called entropy, such that in any process the entropy of an isolated system increases or remains constant, but cannot decrease.*

The thermodynamic definition of entropy is as follows. If an infinitesimal amount of heat dQ is added *reversibly* to a system at temperature T (where T is the absolute temperature of the *system*), then the entropy of the system increases by $dS = dQ/T$. We shall see that this definition (and note that in thermodynamics only entropy *changes* are defined) is consistent with the statistical mechanics definition of entropy $S = k \ln \Omega$ (here the *absolute* value of the entropy is defined).

We have seen already that the law of increasing entropy is a natural consequence of the equation $S = k \ln \Omega$. In some thermodynamics texts (the classic is the book by H.B.Callen) this law is given the status of a postulate or axiom. It may be summarised by $\Delta S \geq 0$.

3.1.2 Restatement of the First Law

Let us now ask what form the first law takes, given this connection between entropy and heat. For an infinitesimal change

$$dE = dQ + dW. \quad \text{this is true always}$$

Taking a fluid ($p - V$ variables) as our thermodynamic system and considering a reversible process we have:

$$dW = -pdV \quad \text{for a reversible process}$$

and also

$$dQ = TdS. \quad \text{for a reversible process}$$

Thus

$$dE = TdS - pdV. \quad \text{for a reversible process}$$

But all the variables in this last expression are *state variables*. In a process connecting two states

$$dE = E_{\text{final}} - E_{\text{initial}} \quad \text{etc.}$$

This does not depend on any details of the process. So we conclude (Finn p86) that for all processes, reversible or irreversible

$$dE = TdS - pdV. \quad \text{always}$$

This form of the first law is very important. You note that all the differentials are exact (i.e. they are differentials of a well defined function). You see that $T = \partial E / \partial S|_V$ in agreement with the statistical definition of temperature.

3.1.3 Microscopic interpretation of the first law

Returning to the microscopic view, the internal energy of a system is given by

$$E = \sum_j p_j \varepsilon_j$$

where p_j is the probability that the system is in the ε_j energy state. So E can change because of changes in ε_j , the energies of the possible quantum states of the system, or changes in p_j , the probability distribution for the system. In an infinitesimal change we can write

$$dE = \sum_j \varepsilon_j dp_j + \sum_j p_j d\varepsilon_j.$$

thermal mechanical

The first term is identified with TdS , the second with $-pdV$. Entropy changes are associated with changes in the occupancies of states, while the mechanical term (work) relates to the energy change of the states. Let us establish this equivalence.

a) Work term

Suppose the energies ε_j , depend on volume (as they do for particles in a box – a gas). Then

$$d\varepsilon_j = \frac{\partial \varepsilon_j}{\partial V} dV.$$

We suppose the derivative to be taken at constant p_j i.e constant S . Then

$$\sum_j p_j d\varepsilon_j = \sum_j p_j \left. \frac{\partial \varepsilon_j}{\partial V} \right|_S dV$$

and since the derivative is taken at constant p_j then the derivative can be taken outside of the sum:

$$\begin{aligned} \sum_j p_j d\varepsilon_j &= \left. \frac{\partial}{\partial V} \right|_S \left(\sum_j p_j \varepsilon_j \right) dV \\ &= \left. \frac{\partial E}{\partial V} \right|_S dV \\ &= -pdV. \end{aligned}$$

Thus we have identified the $\sum_j p_j d\varepsilon_j$ term of dE as the work done on the system.

b) Heat term

The fact that $TdS = \sum_j \varepsilon_j dp_j$ takes a bit longer to prove (see also Guenault p 25, although our approach differs in detail from his; we have already shown $\beta = 1/kT$)

We must make connection with entropy, so we start for the expression for S for the Gibbs ensemble

$$S_{\text{ensemble}} = k \left\{ N \ln N - \sum_j n_j \ln n_j \right\}.$$

This is the entropy for the *ensemble* of N equivalent systems. What we are really interested in is the (mean) entropy of a single system — which of course should be independent of N .

We express the first N as the sum $\sum_j n_j$, so that

$$\begin{aligned}
S_{\text{ensemble}} &= k \left\{ \sum_j n_j \ln N - \sum_j n_j \ln n_j \right\} \\
&= -k \sum_j n_j \ln \left(\frac{n_j}{N} \right).
\end{aligned}$$

Then the (mean) entropy of a single system is one N^{th} of this:

$$S = -k \sum_j \left(\frac{n_j}{N} \right) \ln \left(\frac{n_j}{N} \right)$$

but here we can identify n_j/N as p_j – the probability that a system will be in the j^{th} state. So we have the useful formula for the entropy of a non-isolated system

$$S = -k \sum_j p_j \ln p_j.$$

We shall now use this expression to make the connection between $\sum_j \varepsilon_j dp_j$ and heat. The differential of S is

$$dS = -k \sum_j (dp_j \ln p_j + dp_j).$$

Now the second dp_j sums to zero since the total probability is constant. Thus we have

$$dS = -k \sum_j dp_j \ln p_j$$

and for $\ln p_j$ we shall use the Boltzmann factor

$$p_j = \frac{e^{-\varepsilon_j/kT}}{Z}$$

so that

$$\ln p_j = -\left(\frac{\varepsilon_j}{kT} + Z \right),$$

giving

$$dS = k \sum_j \left(\frac{\varepsilon_j}{kT} + Z \right) dp_j.$$

The second term in the sum is zero since Z is a constant and dp_j sums to zero as above. So only the first term contributes and we obtain

$$dS = \frac{1}{T} \sum_j \varepsilon_j dp_j,$$

or

$$\sum_j \varepsilon_j dp_j = T dS$$

which completes the demonstration.

End of lecture 11

3.1.4 Entropy changes in irreversible processes

We have seen that $dS = \delta Q/T$. And we stated that this applies in a reversible change. In a separate handout we gave some examples of calculating entropy changes.

What happens to the entropy in an irreversible process? To highlight matters let us take an isolated system for which $\delta Q = 0$. Consider a process undergone by this system on removing a constraint. The microscopic understanding of the second law tells us the entropy will increase, as the system goes to the new (more probable) equilibrium macrostate with a larger number of microstates. Since for an isolated system $\delta Q = 0$, the expression $dS = \delta Q/T$ certainly does *not* apply. Indeed, in this case $TdS > \delta Q$. This is generally true for irreversible processes.

Consider a specific example of an irreversible process: the infinitesimal adiabatic free expansion of a gas (by the removal of a partition in a chamber). The partition is the constraint. Replacing the partition will certainly not get us back to the initial state. What will?

In this case

$$\delta Q = 0 \quad \text{and} \quad \delta W = 0$$

so then

$$dE = 0$$

by the first law.

Since the expansion is infinitesimal p is essentially constant, and $p dV > 0$. But we know that

$$dE = TdS - p dV$$

for all processes. Therefore in the free expansion, for which $dE = 0$, if $p dV > 0$, we must correspondingly have $TdS > 0$. So for this irreversible process we find

$$TdS > \delta Q$$

$$-p dV < \delta W.$$

So although no heat has flowed into the system, the entropy has increased. This is a consequence of the irreversible nature of the process.

To summarise:

$$TdS > \delta Q \quad \text{in an irreversible process.}$$

3.2 Alternative statements of the Second Law

3.2.1 Some statements of the Second Law

Now when you read chapter 4 of Finn you will find that the second law is introduced through a discussion of cyclic processes and heat engines. The statement of the law takes a rather different form from the one we have given. That is how the subject developed historically. But we are approaching things from a somewhat different angle. We started from statistical mechanics and the principle of increasing entropy follows easily from that treatment. We'll look at these cyclic processes in a bit.

Here are various statements of the second law:

1a. Heat cannot pass spontaneously from a lower to a higher temperature, while the constraints on the system and the state of the rest of the world are left unchanged.

1b. It is impossible to construct a device that, operating in a cycle, produces no effect other than the transfer of heat from a colder to a hotter body. (Clausius)

2. It is impossible to construct a device that, operating in a cycle, produces no effect other than the extraction of heat from a body and the performance of an equivalent amount of work. (Kelvin-Planck).

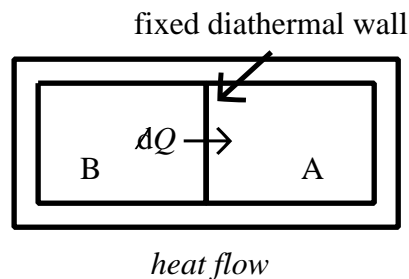
These various statements can be shown to follow from each other (Finn p57) and from the law of increasing entropy.

3.2.2 Demonstration that the law of increasing entropy implies statement 1a

Let us show that $\Delta S \geq 0 \Rightarrow$ statement 1a. (The argument here is identical to that in Section 2.3.3)

Consider two systems A and B separated by a fixed diathermal wall. Thus the volumes of each system are constant, so no work can be done. Since the composite system is thermally isolated $\Delta S \geq 0$. If the two systems are not in thermal equilibrium with each other (i.e. they are at different temperatures) then heat will flow between them.

Consider the exchange of an infinitesimal amount of heat dQ .



The law of entropy increase tells us that

$$\begin{aligned} dS &= dS_A + dS_B \geq 0 \\ &= \left. \frac{\partial S_A}{\partial E_A} \right|_V dE_A + \left. \frac{\partial S_B}{\partial E_B} \right|_V dE_B \\ &= \frac{1}{T_A} dE_A + \frac{1}{T_B} dE_B \end{aligned}$$

since, in general, $1/T = \partial S / \partial E|_V$. Now since no work is done on the system, then

$$dQ = dE_A = -dE_B.$$

Thus

$$dQ \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \geq 0.$$

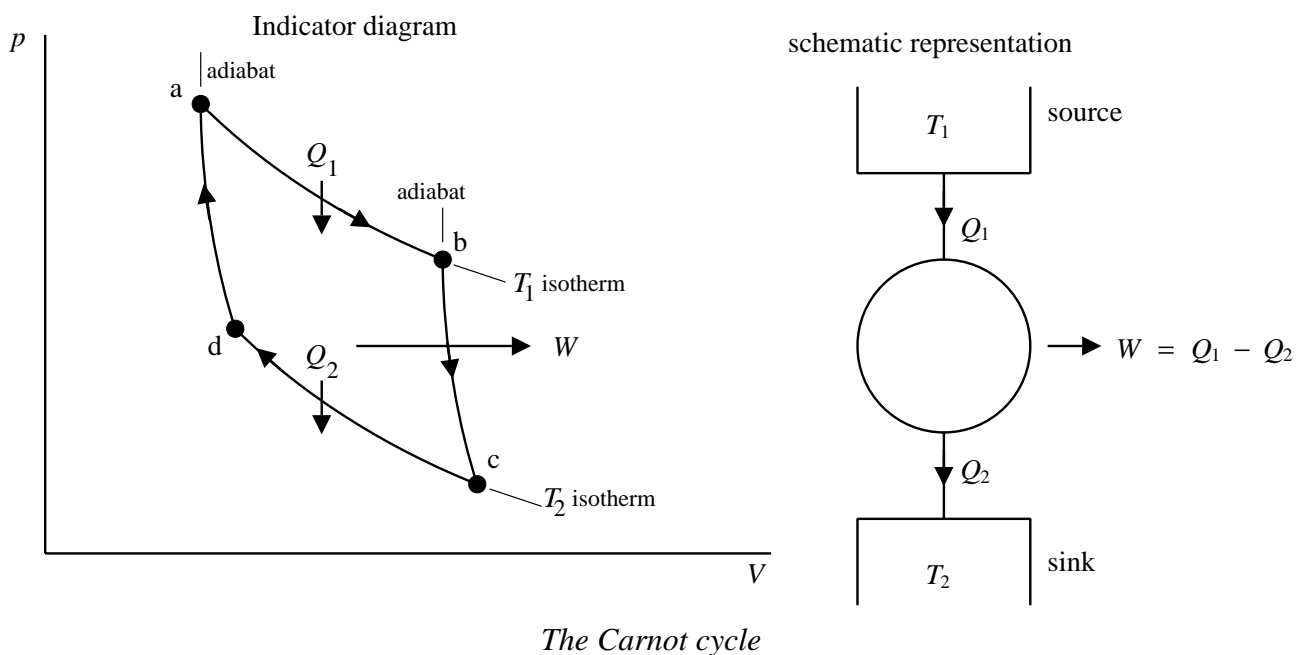
And so then if dQ is positive then this expression implies that $T_A \leq T_B$. So heat must flow spontaneously from hot to cold. This is part of our own experience. Note that we *can* make heat flow from cold to hot if we perform work, a device to do this is called a heat pump (see later).

3.3 The Carnot cycle

3.3.1 Introduction to Carnot cycles — Thermodynamic temperature

The Carnot cycle is an important example of a cyclic process. In such a process the state of the working substance is varied but returns to the original state. So at the end of the cycle the functions of state of the working substance are unchanged. The cycle can be repeated. It thus serves as an idealised model for the operation of real heat engines. It was of practical value at the time of the Industrial Revolution to achieve an understanding of the limitations to the conversion of heat into work. The analysis by Carnot in 1824 was his only publication but a seminal achievement.

We represent the cycle on an indicator diagram as all steps are presumed to be reversible processes. In *one cycle* a quantity of heat Q_1 is taken from a source at high temperature T_1 and Q_2 rejected to a sink at a lower temperature T_2 .



The Carnot cycle

Since the process is cyclic the working substance returns to its initial state. And since E and S are both functions of state it follows that

$$\Delta E = 0 \quad \text{and} \quad \Delta S = 0.$$

Since for the working substance $\Delta E = 0$ then the first law tells us

$$W = Q_1 - Q_2.$$

Now the whole system, including the reservoirs, is isolated. So according to our statement of the second law

$$\Delta S_{\text{total}} \geq 0.$$

So

$$\Delta S_1 + \Delta S_2 + \Delta S \geq 0;$$

the total entropy change is the sum of that of reservoirs 1 and 2 and that of the system.

Since

$$\begin{aligned}\Delta S &= 0, \\ \Delta S_1 &= -Q_1/T_1 \\ \Delta S_2 &= Q_2/T_2.\end{aligned}$$

Then

$$-\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \geq 0.$$

Now imagine that the cycle is operated backwards. Now we have a heat pump. The analysis is identical except

$$Q_1 \rightarrow -Q_1, \quad Q_2 \rightarrow -Q_2.$$

Then the law of entropy increase tells us that

$$-\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \leq 0.$$

It is clear that the equality must hold in such a reversible cycle. So then

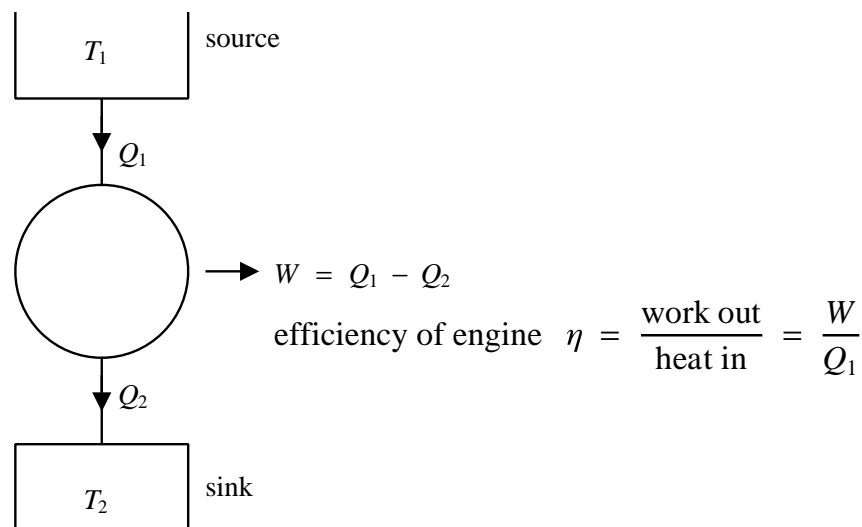
$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}.$$

In thermodynamics texts this is taken to be the definition of the thermodynamic temperature scale. By taking the working substance to be an ideal gas we may show the identity of this temperature scale with the ideal gas scale.

End of lecture 12

3.3.2 Efficiency of heat engines and heat pumps

The efficiency of an engine characterises how well the engine transforms heat into work.



a heat engine

Since $W = Q_1 - Q_2$ it follows that the efficiency of a Carnot engine depends *only on the temperature of the reservoirs*.

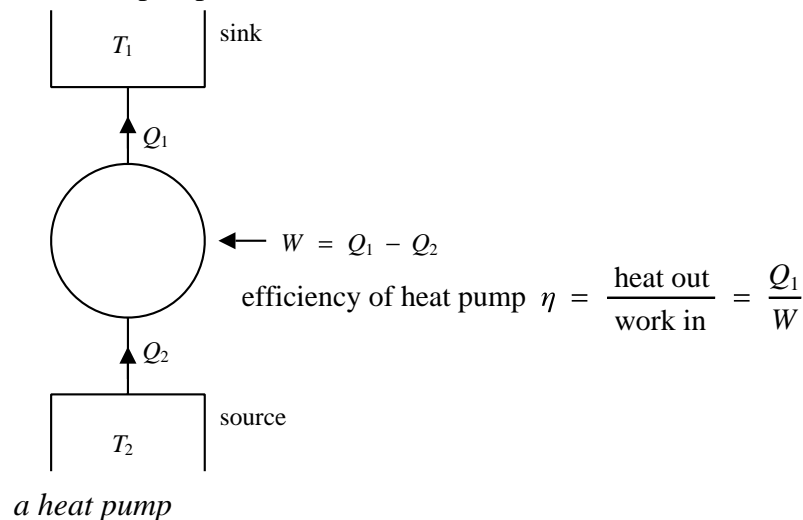
$$\begin{aligned}\eta &= \frac{Q_1 - Q_2}{Q_1} \\ &= 1 - \frac{Q_2}{Q_1} \\ &= 1 - \frac{T_2}{T_1}.\end{aligned}$$

The significance of this result is that the efficiency depends only on the choice of reservoir temperatures (and not on the choice of working substance).

It may be shown (Finn p59) that no engine operating between the same two reservoirs can be more efficient than a Carnot engine and that all reversible engines operating between the same two reservoirs are equally efficient.

In practical engines T_2 is fixed (near ambient temperature) so in order to increase η we must increase T_1 by, for example, the use of superheated steam. Note that in principle 100% efficiency would be achievable for $T_2 = 0$. The unattainability of absolute zero: the third law of thermodynamics, disallows this however.

A heat pump is a heat engine operating in reverse. In this case work is done *on* the working substance, and as a consequence heat is pumped from a cooler reservoir to a hotter one.



As an example of a heat pump, the Festival Hall is heated from the (cooler) River Thames. You see that the efficiency of a heat pump is different from that of a heat engine. In fact the efficiency of a heat pump will *always* be greater than 100%! Otherwise we may as well just use an electric heater and get just 100%. The efficiency of a Carnot heat pump is given by

$$\begin{aligned}\eta &= \frac{Q_1}{Q_1 - Q_2} \\ &= \frac{1}{1 - T_2/T_1};\end{aligned}$$

it also depends only on the initial and final temperatures. Observe that the efficiency is greatest when the initial and final temperatures are close together. For this reason heat pumps are best used for providing low-level background heating.

3.3.3 Equivalence of ideal gas and thermodynamic temperatures

Thus far we have seen that our originally introduced *statistical temperature*, defined by

$$\frac{1}{T} = \left. \frac{\partial S}{\partial V} \right|_{\text{no work}}$$

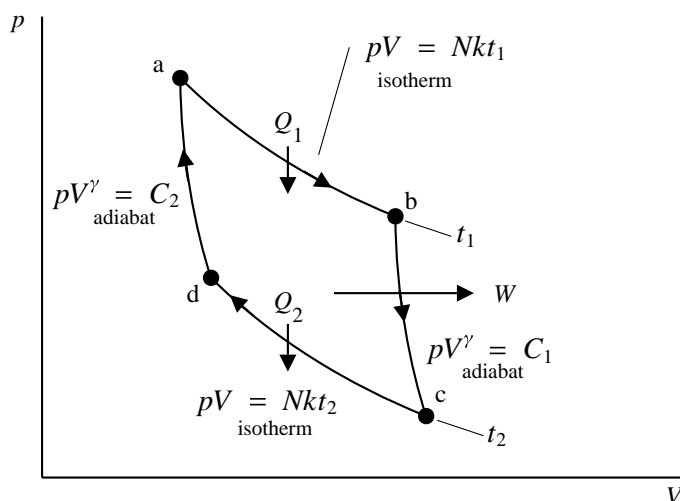
is equivalent to *thermodynamic temperature*, defined by

$$\frac{T_2}{T_1} = \frac{Q_2}{Q_1},$$

the heat ratio for a Carnot cycle. In this section we will demonstrate the equivalence with the ideal gas temperature. For clarity we denote the ideal gas temperature by t ; we take the ideal gas equation of state as

$$pV = Nkt$$

and our task is to calculate the heat ratio for a Carnot cycle having a working substance which obeys this equation of state.



ideal gas Carnot cycle

Two other properties of the ideal gas will be used. We have the adiabatic equation

$$pV^\gamma = \text{const.}$$

and we will use the fact that the internal energy of an ideal gas depends only on its temperature; in particular, E will remain constant along an isotherm.

The cycle consists of four steps:

- 1 $a \rightarrow b$ During the isothermal expansion $a \rightarrow b$ heat Q_1 is taken in at constant temperature t_1 . The internal energy is constant during this step, so the work done *on* the system is minus the heat flow Q_1 *into* the system.
- 2 $b \rightarrow c$ During the adiabatic expansion $b \rightarrow c$ there is no heat flow, but the gas is cooled from temperature t_1 to temperature t_2 .
- 3 $c \rightarrow d$ During the isothermal compression $c \rightarrow d$ heat Q_2 is given out at constant temperature t_2 . The internal energy is constant during this step, so the work done *on* the system is equal to the heat flow Q_1 *into* the system.

4 d → a During the adiabatic compression d → a there is no heat flow, but the gas is warmed from temperature t_2 up to the starting temperature t_1 . The initial state has been recovered.

We must calculate the heat flows in steps 1 and 3.

In step 1 the heat flow Q_1 into the system is minus the work done on the system:

$$Q_1 = + \int_{V_a}^{V_b} p \, dV$$

but the path is an isotherm so that p is given by

$$p = \frac{1}{V} Nkt_1.$$

Integrating up the expression for Q_1 we then find

$$Q_1 = Nkt_1 \int_{V_a}^{V_b} \frac{dV}{V}$$

or

$$Q_1 = Nkt_1 \ln \frac{V_b}{V_a}.$$

In step 3 the heat flow Q_2 out of the system is equal to the work done on the system:

$$Q_2 = - \int_{V_c}^{V_d} p \, dV$$

but the path is an isotherm so that p is given by

$$p = \frac{1}{V} Nkt_2.$$

Integrating up the expression for Q_2 we then find

$$Q_2 = -Nkt_2 \int_{V_c}^{V_d} \frac{dV}{V}$$

or

$$Q_2 = Nkt_2 \ln \frac{V_c}{V_d}.$$

And the ratio of the heats in and out is then

$$\frac{Q_1}{Q_2} = \frac{t_1}{t_2} \frac{\ln V_b/V_a}{\ln V_c/V_d}.$$

The ratio t_1/t_2 looks promising, but we must now find the expressions for the volumes.

First we summarise the simultaneous relations between p and V at the points a, b, c, d.

$$\begin{array}{ll} \text{a :} & p_a V_a = Nkt_1 \quad , \quad p_a V_a^\gamma = C_2 \\ \text{b :} & p_b V_b = Nkt_1 \quad , \quad p_b V_b^\gamma = C_1 \\ \text{c :} & p_c V_c = Nkt_2 \quad , \quad p_c V_c^\gamma = C_1 \\ \text{d :} & p_d V_d = Nkt_2 \quad , \quad p_d V_d^\gamma = C_2. \end{array}$$

To eliminate the p s let us divide each second (adiabatic) equation by the corresponding first

(isothermal). This gives

$$V_a^{\gamma-1} = C_2 / Nkt_1$$

$$V_b^{\gamma-1} = C_1 / Nkt_1$$

$$V_c^{\gamma-1} = C_1 / Nkt_2$$

$$V_d^{\gamma-1} = C_2 / Nkt_2$$

and we then have the results

$$V_b / V_a = (C_1 / C_2)^{\frac{1}{\gamma-1}}$$

$$V_c / V_d = (C_1 / C_2)^{\frac{1}{\gamma-1}}.$$

These two expressions are equal so that

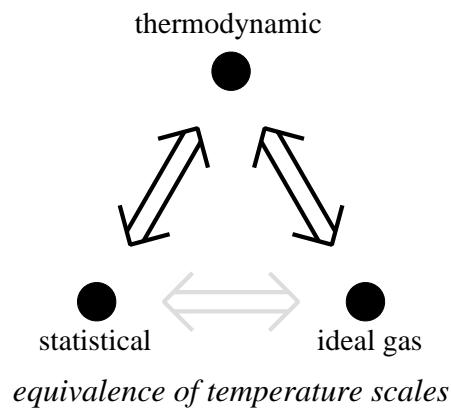
$$\frac{\ln V_b / V_a}{\ln V_c / V_d} = 1,$$

giving the result

$$\frac{Q_1}{Q_2} = \frac{t_1}{t_2}$$

relating the heat input and output for an ideal gas Carnot cycle to the *ideal gas* temperature. But the identical relation was used as an operational definition of *thermodynamic* temperature. Thus we have demonstrated the equivalence of the ideal gas and the thermodynamic temperature scales (to within a multiplicative constant).

Recall that our definition of thermodynamic temperature followed from our definition of *statistical* temperature. So in reality we now have the equivalence of the ideal gas, thermodynamic, and statistical temperatures.



Logically there is no need to complete the triangle and prove directly that the statistical and ideal gas scales are equivalent, but we will do that when studying the statistical mechanics of the ideal gas.

End of lecture 13

3.4 Thermodynamic potentials

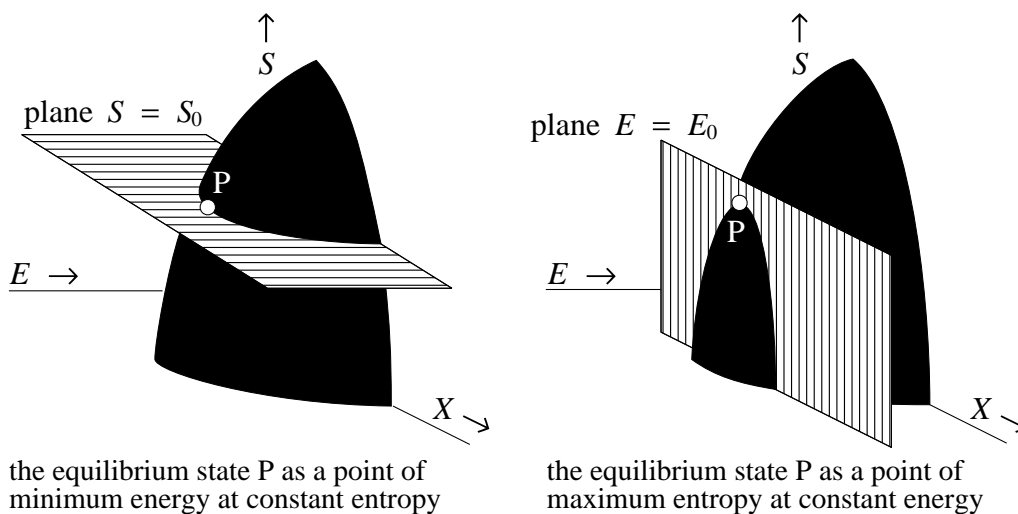
3.4.1 Equilibrium states

We have seen that the equilibrium state of an isolated system – characterised by E , V , N – is determined by maximising the entropy S . On the other hand we know that a purely mechanical system settles down to the equilibrium state which minimises the energy: the state where the forces $F_i = -\partial E / \partial x_i$ vanish. In this section we shall see how to relate these two ideas. And then in the following sections we shall see how to extend the ideas.

By a purely mechanical system we mean one with *no* thermal degrees of freedom. This means no changing of the *populations* of the different quantum states – i.e. at constant entropy. But this should also apply for a thermodynamic system at constant entropy. So we should be able to find the equilibrium state in two ways:

- Maximise the entropy at constant energy.
- Minimise the energy at constant entropy.

That these approaches are equivalent may be seen by considering the state of the $E - S - X$ surface for a system. Here X is some extensive quantity that will vary when the system approaches equilibrium like the energy in or the number of particles in one half of the system.



alternative specification of equilibrium states

At constant energy the plane $E = E_0$ intersects the $E S X$ surface along a line of possible states of the system. We have seen that the equilibrium state – the state of maximum probability – will be the point of maximum entropy: the point P on the curve.

But now consider the same system at constant entropy. The plane $S = S_0$ intersects the $E S X$ surface along a different line of possible states. Comparing the two pictures we see that the equilibrium point P is now the point of minimum energy.

Equivalence of the entropy maximum and the energy minimum principles depends on the shape of the $E S X$ surface. In particular, it relies on

- a) S having a maximum with respect to X – guaranteed by the second law,
- b) S being an increasing function of E
 - $\partial S / \partial E = 1 / T > 0$ means positive temperatures
- c) E being a single-valued continuous function of S .

To demonstrate the equivalence of the entropy maximum and the energy minimum principles we shall show that the converse would lead to a violation of the second law.

Assume that the energy E is *not* the minimum value consistent with a given entropy S . Then let us take some energy out of the system in the form of work and return it in the form of heat. The energy is then the same but the entropy will have increased. So the original state could not have been an equilibrium state.

The equivalence of the energy minimum and the entropy maximum principle is rather like describing the circle as having the maximum area at fixed circumference or the minimum circumference for a given area.

We shall now look at the specification of equilibrium states when instead of energy or entropy, other variables are held constant.

3.4.2 Constant temperature (and volume): the Helmholtz potential

To maintain a system of fixed volume at constant temperature we shall put it in contact with a heat reservoir. The equilibrium state can be determined by maximising the total entropy while keeping the total energy constant.

The total entropy is the sum of the system entropy and that of the reservoir. The entropy maximum condition is then

$$\left. \begin{aligned} dS_T &= dS + dS_{\text{res}} = 0 \\ d^2S_T &< 0. \end{aligned} \right\}$$

The entropy differential for the reservoir is

$$\begin{aligned} dS_{\text{res}} &= \frac{dE_{\text{res}}}{T_{\text{res}}} \\ &= -\frac{dE}{T} \end{aligned}$$

since the total energy is constant. The total entropy maximum condition is then

$$\left. \begin{aligned} dS - \frac{dE}{T} &= 0 \\ d^2S - \frac{d^2E}{T} &< 0. \end{aligned} \right\}$$

Or, since T is constant,

$$\left. \begin{aligned} d(E - TS) &= 0 \\ d^2(E - TS) &> 0, \end{aligned} \right\}$$

which is the condition for a minimum in $E - TS$. But we have encountered $E - TS$ before, in the consideration of the link between the partition function and thermodynamic properties. This function is the Helmholtz free energy F . So we conclude that

at constant N, V and T , $F = E - TS$ is a minimum

— The Helmholtz minimum principle.

We can understand this as a competition between two opposing effects. At high temperatures the entropy tends to a maximum, while at low temperatures the energy tends to a minimum. And the balance between these competing processes is given, at general temperatures, by minimising the combination $F = E - TS$.

• 3.4.3 Constant pressure and energy: the Enthalpy function

To maintain a system at constant pressure we shall put it in mechanical contact with a “volume reservoir”. That is, it will be connected by a movable, thermally isolated piston, to a very large volume. As before, we can determine the equilibrium state by maximising the total entropy while keeping the total energy constant. Alternatively and equivalently, we can keep the total entropy constant while minimising the total energy.

The energy minimum condition is

$$\left. \begin{aligned} dE_T &= dE + dE_{\text{res}} = 0 \\ d^2E_T &> 0. \end{aligned} \right\}$$

In this case the reservoir may do mechanical work on our system:

$$dE_{\text{res}} = -p_{\text{res}}dV_{\text{res}} = pdV$$

since the total volume is fixed. We then write the energy minimum condition as

$$\left. \begin{aligned} dE + pdV &= 0 \\ d^2E + pd^2V &> 0, \end{aligned} \right\}$$

or, since p is constant

$$\left. \begin{aligned} d(E + pV) &= 0 \\ d^2(E + pV) &> 0. \end{aligned} \right\}$$

This is the condition for a minimum in $E + pV$. This function is called the Enthalpy, and it is given the symbol H . So we conclude that

at constant N, p and E , $H = E + pV$ is a minimum

— The Enthalpy minimum principle.

• 3.4.4 Constant pressure and temperature: the Gibbs free energy

In this case our system can exchange both thermal and mechanical energy with a reservoir; both heat energy and “volume” may be exchanged. Working in terms of the minimum energy at constant entropy condition for the combined system + reservoir

$$\left. \begin{aligned} dE_T &= dE + dE_{\text{res}} = 0 \\ d^2E_T &> 0. \end{aligned} \right\}$$

In this case the reservoir give heat energy and/or it may do mechanical work on our system:

$$dE_{\text{res}} = T_{\text{res}}dS_{\text{res}} - p_{\text{res}}dV_{\text{res}} = -TdS + pdV$$

since the total energy is fixed. We then write the energy minimum condition as

$$\left. \begin{aligned} dE - TdS + pdV &= 0 \\ d^2E - Td^2S + pd^2V &> 0, \end{aligned} \right\}$$

or, since T and p are constant

$$\left. \begin{aligned} d(E - TS + pV) &= 0 \\ d^2(E - TS + pV) &> 0. \end{aligned} \right\}$$

This is the condition for a minimum in $E - TS + pV$. This function is called the Gibbs free energy, and it is given the symbol G . So we conclude that

at constant N, p and T , $G = E - TS + pV$ is a minimum

— The Gibbs free energy minimum principle.

3.4.5 Differential expressions for the potentials

The internal energy, Helmholtz free energy, enthalpy and Gibbs free energy are called *thermodynamic potentials*. Clearly they are all functions of state. From the definitions

$$F = E - TS \quad \text{Helmholtz function}$$

$$H = E + pV \quad \text{Enthalpy function}$$

$$G = E - TS + pV \quad \text{Gibbs function}$$

and the differential expression for the internal energy

$$dE = TdS - pdV$$

we obtain the differential expressions for the potentials:

$$dF = -SdT - pdV$$

$$dH = TdS + Vdp$$

$$dG = -SdT + Vdp.$$

Considering the differentials as *virtual changes*, i.e. the system “feeling out” the situation in the neighbourhood of the equilibrium state, we immediately see that

- at fixed S and V , $dS = 0$ and $dV = 0$ so that $dE = 0 \Rightarrow E$ is minimised
- at fixed T and V , $dT = 0$ and $dV = 0$ so that $dF = 0 \Rightarrow F$ is minimised
- at fixed S and p , $dS = 0$ and $dp = 0$ so that $dH = 0 \Rightarrow H$ is minimised
- at fixed T and p , $dT = 0$ and $dp = 0$ so that $dG = 0 \Rightarrow G$ is minimised.

This summarises compactly the extremum principles obtained in the previous section.

3.4.6 Natural variables and the Maxwell relations

Each of the thermodynamic potentials has its own *natural variables*. For instance, taking E , the differential expression for the first law is

$$dE = TdS - pdV.$$

Thus if E is known as a function of S and V then everything else – like T and p – can be obtained by differentiation, since $T = \partial E / \partial S|_V$ and $p = - \partial E / \partial V|_S$. If, instead, E were known as a function of, say, T and V , then we would need more information like an equation of state to completely determine the remaining thermodynamic functions.

All the potentials have their natural variables in terms of which the dependent variables may be found by differentiation:

$$\begin{aligned} E(S, V), \quad dE &= TdS - pdV, & T &= \left. \frac{\partial E}{\partial S} \right|_V, & p &= - \left. \frac{\partial E}{\partial V} \right|_S, \\ F(T, V), \quad dF &= -SdT - pdV, & S &= - \left. \frac{\partial F}{\partial T} \right|_V, & p &= - \left. \frac{\partial F}{\partial V} \right|_T, \\ H(S, p), \quad dH &= TdS + Vdp, & T &= \left. \frac{\partial H}{\partial S} \right|_p, & V &= \left. \frac{\partial H}{\partial p} \right|_S, \\ G(T, p), \quad dG &= -SdT + Vdp, & S &= - \left. \frac{\partial G}{\partial T} \right|_p, & V &= \left. \frac{\partial G}{\partial p} \right|_T. \end{aligned}$$

If we differentiate one of these results with respect to a further variable then the order of differentiation is immaterial; differentiation is commutative. Thus, for instance, using the energy natural variables we see that

$$\left. \frac{\partial}{\partial V} \right|_S \left. \frac{\partial}{\partial S} \right|_V = \left. \frac{\partial}{\partial S} \right|_V \left. \frac{\partial}{\partial V} \right|_S,$$

and operating on E with this we obtain

$$\begin{aligned} \left. \frac{\partial}{\partial V} \right|_S \left. \frac{\partial E}{\partial S} \right|_V &= \left. \frac{\partial}{\partial S} \right|_V \left. \frac{\partial E}{\partial V} \right|_S \\ \parallel & \qquad \qquad \parallel \\ T & \qquad \qquad -p \end{aligned}$$

so that we obtain the result

$$\left. \frac{\partial T}{\partial V} \right|_S = - \left. \frac{\partial p}{\partial S} \right|_V.$$

Similarly, we get one relation for each potential by differentiating it with respect to its two natural variables

$$\begin{aligned} E & \quad \left. \frac{\partial T}{\partial V} \right|_S = - \left. \frac{\partial p}{\partial S} \right|_V \\ F & \quad \left. \frac{\partial S}{\partial T} \right|_V = \left. \frac{\partial p}{\partial T} \right|_V \\ H & \quad \left. \frac{\partial T}{\partial p} \right|_S = \left. \frac{\partial V}{\partial S} \right|_p \\ G & \quad \left. \frac{\partial S}{\partial p} \right|_T = - \left. \frac{\partial V}{\partial T} \right|_p. \end{aligned}$$

The Maxwell relations give equations between seemingly different quantities. In particular, they often connect easily measured, but uninteresting quantities to difficult-to-measure, but very interesting ones.

End of lecture 14

3.5 Some applications

3.5.1 Entropy of an ideal gas

We want to obtain an expression for the entropy of an ideal gas. Of course the mathematical expression will depend on the choice of independent variables. We take as independent variables temperature and volume (the natural variables of the canonical distribution or F).

There is a function $S(T, V)$, that we want to find. We shall do this by taking the differential of this, identifying the coefficients, and then integrating up. So we start from

$$dS = \left. \frac{\partial S}{\partial T} \right|_V dT + \left. \frac{\partial S}{\partial V} \right|_T dV.$$

The first coefficient is seen to be related to the thermal capacity, since

$$C_V = T \left. \frac{\partial S}{\partial T} \right|_V.$$

The second coefficient can be transformed with a Maxwell relation

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial p}{\partial T} \right|_V$$

and the derivative on the right hand side may be found from the equation of state:

$$p = \frac{NkT}{V}$$

so that

$$\left. \frac{\partial p}{\partial T} \right|_V = \frac{Nk}{V}.$$

then the differential of S becomes

$$dS = \frac{C_V}{T} dT + \frac{Nk}{V} dV.$$

The second term can be integrated immediately. And on the assumption that C_V is a constant, the first term also can be integrated. In this case we find

$$S = C_V \ln T + Nk \ln V + S_0$$

where S_0 is a constant. Note that from purely macroscopic considerations the entropy can not be determined absolutely; there is always an arbitrary constant. Furthermore beware of considering separate terms of this expression separately. It makes no sense to ascribe one contribution to the entropy from the temperature and another from the volume; these will change upon changing temperature and volume units. What is well-defined is entropy *changes*. Writing

$$S_2 - S_1 = C_V \ln \frac{T_2}{T_1} + Nk \ln \frac{V_2}{V_1}$$

the arguments of the logarithms are dimensionless and then no ambiguity occurs in ascribing different contributions to the different terms of the equation.

We also note that the microscopic approach will give an expression of the above form, with a well-defined value for the arbitrary constant. For a monatomic gas we will see later on that statistical mechanics will give us the result

$$S = \frac{3}{2}Nk \ln T + Nk \ln V + \frac{3}{2}Nk \ln \frac{mk}{2\pi\hbar^2} - Nk \ln N + \frac{5}{2}Nk,$$

sometimes called the Sackur-Tetrode equation. The first two terms give the $\ln T$ and $\ln V$ terms as before where, of course, for the monatomic gas $C_V = \frac{3}{2}Nk$. The last three terms give an absolute value for the constant S_0 . A microscopic parameter enters here in the mass m of the particles.

3.5.2 General expression for $C_p - C_V$

The thermal capacity of an object is found by measuring the temperature rise when a small quantity of heat is applied. It is much easier to do this while keeping the body at constant pressure (possibly atmospheric pressure), than at constant volume. However if we are calculating the properties of a system then this is much easier done at constant volume, when the energy levels do not change. The relation between these two thermal capacities provides a nice example of the use of Maxwell relations.

We know that for an ideal gas the difference between the thermal capacities is given by

$$C_p - C_V = Nk.$$

This is not true for a general system. Here we shall investigate the relation for a real gas. We start from the expression for C_V :

$$C_V = T \left. \frac{\partial S}{\partial T} \right|_V$$

which suggests we should consider the entropy as a function of T and V (as we did above). The differential of $S(T, V)$ is

$$\begin{aligned} dS &= \left. \frac{\partial S}{\partial T} \right|_V dT + \left. \frac{\partial S}{\partial V} \right|_T dV \\ &= \frac{C_V}{T} dT + \left. \frac{\partial S}{\partial V} \right|_T dV. \end{aligned}$$

What we want to find is C_p :

$$C_p = T \left. \frac{\partial S}{\partial T} \right|_p$$

which suggests we divide the dS equation by dT at constant pressure. This gives

$$\left. \frac{\partial S}{\partial T} \right|_p = \frac{C_V}{T} + \left. \frac{\partial S}{\partial V} \right|_T \left. \frac{\partial V}{\partial T} \right|_p,$$

or

$$C_p - C_V = T \left. \frac{\partial S}{\partial V} \right|_T \left. \frac{\partial V}{\partial T} \right|_p.$$

Ideally, this expression should be related to readily-measurable quantities. Now the $\partial V / \partial T$ term is connected with the thermal expansion coefficient, but the $\partial S / \partial V$ term is not so easily understood; entropy is not easy to measure. However a Maxwell relation will rescue us:

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial p}{\partial T} \right|_V,$$

so that

$$C_p - C_v = T \left. \frac{\partial p}{\partial T} \right|_V \left. \frac{\partial V}{\partial T} \right|_p.$$

The readily available quantities are usually the isobaric expansion coefficient β_p

$$\beta_p = \frac{1}{V} \left. \frac{\partial V}{\partial T} \right|_p$$

and the isothermal compressibility k_T

$$k_T = -\frac{1}{V} \left. \frac{\partial V}{\partial p} \right|_T.$$

This last expression may be transformed using the cyclic rule of partial differentiation

$$\left. \frac{\partial x}{\partial y} \right|_z \left. \frac{\partial y}{\partial z} \right|_x \left. \frac{\partial z}{\partial x} \right|_y = -1$$

and the reciprocal rule

$$\left. \frac{\partial x}{\partial y} \right|_z = \frac{1}{\left. \frac{\partial y}{\partial x} \right|_z}.$$

So we can write the $\partial p / \partial T$ term as

$$\left. \frac{\partial p}{\partial T} \right|_V = - \left. \frac{\partial V}{\partial T} \right|_p \left. \frac{\partial p}{\partial V} \right|_T.$$

This enables us to express the difference in the thermal capacities as

$$C_p - C_v = -T \left. \frac{\partial V}{\partial T} \right|_p^2 \left. \frac{\partial p}{\partial V} \right|_T$$

or

$$C_p - C_v = \frac{TV\beta_p^2}{k_T}.$$

This is actually quite an important result. From this equation a number of deductions follow:

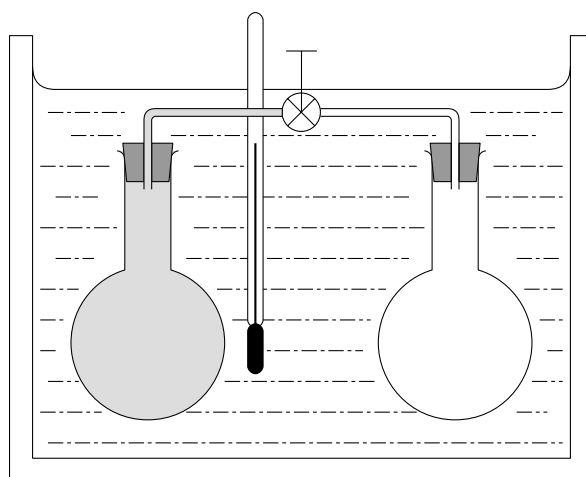
- Since k must be positive (stability requirement) and β^2 will be positive it follows that C_p can never be less than C_v .
- The thermal capacities will become equal as $T \rightarrow 0$.
- At finite temperatures the thermal capacities will become equal when the expansion coefficient becomes zero: a maximum or minimum in density. Water at 4°C is an example.

End of lecture 15

3.5.3 Joule Expansion – ideal gas

Joule wanted to know how the internal energy of a gas depended on its volume. Clearly this is related to the interactions between the molecules and how this varies with their separation.

Joule had two containers joined by a tap. One container had air at a high pressure and the other was evacuated. The whole assembly was placed in a bucket of water and Joule looked for a change in the temperature of the system when the tap was opened.



Joule's experiment

As we have seen already, when the tap is opened the subsequent process is irreversible. We cannot follow the evolution of the system, but once things have settled down and the system has come to an equilibrium, we can consider the various functions of state and we can construct any convenient reversible path between these states. In this case, since the assembly is isolated, the internal energy will be unchanged.

So writing E as a function of temperature and volume, its differential is

$$dE = \left. \frac{\partial E}{\partial V} \right|_T dV + \left. \frac{\partial E}{\partial T} \right|_V dT.$$

But since the internal energy remains unchanged, $dE = 0$, it follows that

$$\left. \frac{\partial E}{\partial V} \right|_T dV + \left. \frac{\partial E}{\partial T} \right|_V dT = 0.$$

Now in his experiments Joule could not detect any temperature change. So he concluded that

$$\left. \frac{\partial E}{\partial V} \right|_T = 0.$$

That is, he deduced that while the internal energy might depend on temperature, it *cannot* depend on the volume. This meant that the energy of the molecules was independent of their separation – in other words, no forces of interaction. And of course with hindsight, we understand an ideal gas as one with negligible interactions between the particles.

In fact Joule's experiment was extremely insensitive because of the thermal capacity of the surroundings. This tended to reduce the magnitude of any possible temperature change. Rather than a single-shot experiment, greater sensitivity could be obtained with a continuous flow experiment. Before considering this, however, we shall examine the Joule experiment for a real, non-ideal gas.

3.5.4 Joule Expansion – real non-ideal gas

A real gas does have interactions between the constituent particles. So in a free expansion there might well be a temperature change. Although the process is fundamentally irreversible, in line with our previous discussion, we can evaluate functions of state by taking any reversible path between the initial and final states.

The free expansion occurs at constant internal energy. When the volume increases by ΔV there may

be a temperature increase ΔT and to quantify this we introduce the Joule coefficient α_J :

$$\alpha_J = \left. \frac{\partial T}{\partial V} \right|_E.$$

We want to relate this coefficient to the behaviour of a real gas, involving such things as a realistic equation of state.

In evaluating α_J the first thing we observe is that the derivative is taken at constant internal energy. This is a little awkward to handle in realistic calculations, so let us transform it away using the cyclical rule

$$\left. \frac{\partial T}{\partial V} \right|_E \left. \frac{\partial E}{\partial T} \right|_V \left. \frac{\partial V}{\partial E} \right|_T = -1$$

so that

$$\left. \frac{\partial T}{\partial V} \right|_E = - \left. \frac{\partial T}{\partial E} \right|_V \left. \frac{\partial E}{\partial V} \right|_T$$

or

$$\alpha_J = -\frac{1}{C_V} \left. \frac{\partial E}{\partial V} \right|_T.$$

Now since we know

$$dE = TdS - pdV$$

it follows that

$$\left. \frac{\partial E}{\partial V} \right|_T = T \left. \frac{\partial S}{\partial V} \right|_T - p$$

and the derivative here may be transformed using a Maxwell relation:

$$\left. \frac{\partial E}{\partial V} \right|_T = T \left. \frac{\partial p}{\partial T} \right|_V - p$$

giving, finally,

$$\alpha_J = -\frac{1}{C_V} \left[T \left. \frac{\partial p}{\partial T} \right|_V - p \right].$$

We may represent the equation of state of a real gas by a *virial expansion* (an expansion in powers of the density):

$$\frac{p}{kT} = \frac{N}{V} + B_2(T) \left(\frac{N}{V} \right)^2 + B_3(T) \left(\frac{N}{V} \right)^3 + \dots$$

The B factors are called *virial coefficients*; B_n is the n^{th} virial coefficient.

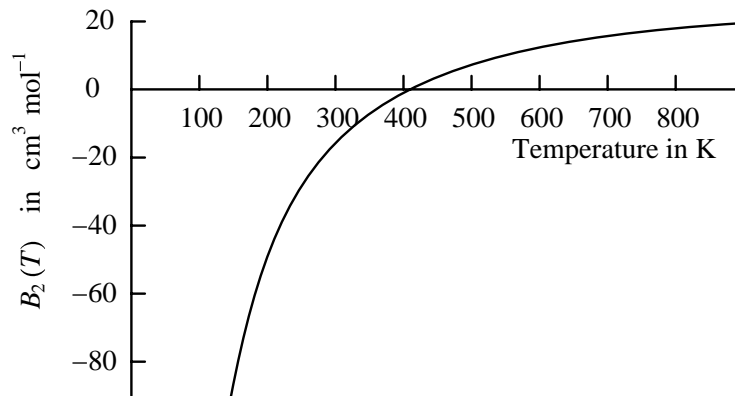
The derivative is evaluated as

$$\left. \frac{\partial p}{\partial T} \right|_V = k \frac{N}{V} + kB_2(T) \left(\frac{N}{V} \right)^2 + kT \frac{dB_2(T)}{dT} \left(\frac{N}{V} \right)^2 + \dots$$

giving the Joule coefficient, to leading order in density

$$\alpha_J = -\frac{1}{C_V} kT^2 \frac{dB_2(T)}{dT} \left(\frac{N}{V} \right)^2;$$

the smaller higher order terms have been neglected.



second virial coefficient for argon

As an example, for argon at 0°C, $dB_2/dT = 0.25 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$, and $C_V = \frac{3}{2}Nk$, giving α_J as

$$\alpha_J = -2.5 \times 10^{-5} \text{ K mol cm}^{-3}.$$

The temperature change in a finite free expansion is found by integrating:

$$\Delta T = \int_{V_1}^{V_2} \alpha \, dV.$$

For one mole of argon at STP, if we double its volume the temperature will drop by only 0.6 K. This was too small for Joule to measure.

Free expansion always results in cooling. Temperature is a measure of the kinetic energy of the molecular motion. On expansion the mean spacing of the molecules increases. The attractive tail of the interparticle interaction then gets weaker, tending to zero from its negative value. Since the free expansion takes place at constant E , or total energy, this increase in potential energy is accompanied by a corresponding decrease in kinetic energy. So the temperature decreases.

Incidentally, we note from the relation

$$\alpha_J = -\frac{1}{C_V} \left. \frac{\partial E}{\partial V} \right|_T$$

and our result for α_J :

$$\alpha_J = -\frac{1}{C_V} \left[T \left. \frac{\partial p}{\partial T} \right|_V - p \right]$$

that for a gas obeying the ideal gas equation of state

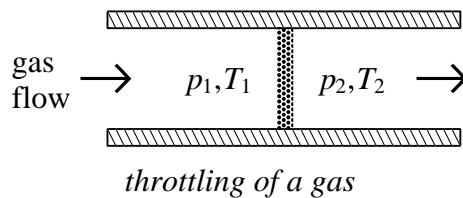
$$\left. \frac{\partial E}{\partial V} \right|_T = 0.$$

In other words we have demonstrated that for an ideal gas the internal energy is a function only of its temperature.

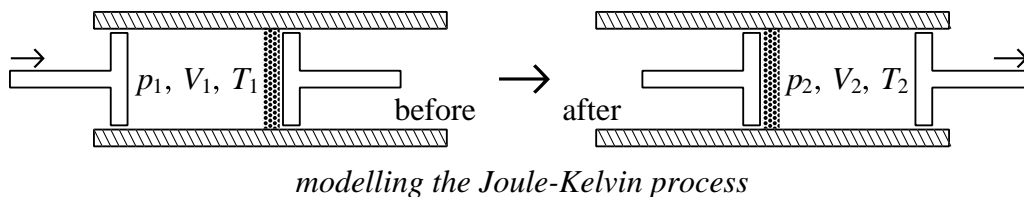
3.5.5 Joule-Kelvin or Joule-Thomson process – Throttling

「The names Kelvin and Thomson refer to the same person; William Thomson became Lord Kelvin.」

In a throttling process a gas is forced through a flow impedance such as a porous plug. For a continuous process, in the steady state, the pressure will be constant (but different) either side of the impedance. As this is a continuous flow process the walls of the container will be in equilibrium with the gas; their thermal capacity is thus irrelevant. Such a throttling process, where heat neither enters nor leaves the system is referred to as a Joule-Kelvin or Joule Thomson process.



This is fundamentally an irreversible process, but the arguments of thermodynamics are applied to such a system simply by considering the equilibrium initial state and the equilibrium final state which applied way before and way after the actual process. To study this throttling process we shall focus attention on a fixed mass of the gas. We can then regard this portion of the gas as being held between two moving pistons. The pistons move so as to keep the pressures p_1 and p_2 constant.



Work must be done to force the gas through the plug. The work done is

$$\Delta W = - \int_{V_1}^0 p_1 dV - \int_0^{V_2} p_2 dV = p_1 V_1 - p_2 V_2 .$$

Since the system is thermally isolated the change in the internal energy is due entirely to the work done:

$$E_2 - E_1 = p_1 V_1 - p_2 V_2$$

or

$$E_1 + p_1 V_1 = E_2 + p_2 V_2 .$$

The *enthalpy* H is defined by

$$H = E + pV$$

so we conclude that in a Joule-Kelvin process the enthalpy is conserved.

The interest in the throttling process is that whereas for an ideal gas the temperature remains constant, it is possible to have either cooling or warming when the process happens to a non-ideal gas. — The operation of most refrigerators is based on this. By contrast, with Joule expansion one only has cooling.

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3.5.6 Joule-Thomson coefficient

The fundamental differential relation for the enthalpy is

$$dH = TdS + Vdp$$

and dH is zero for this process. It is, however, rather more convenient to use T and p as the independent variables rather than the natural S and p , since ultimately we want to relate dT to dp . This is effected by expressing dS is expressed in terms of dT and dp :

$$dS = \left. \frac{\partial S}{\partial T} \right|_p dT + \left. \frac{\partial S}{\partial p} \right|_T dp.$$

But

$$\left. \frac{\partial S}{\partial T} \right|_p = \frac{C_p}{T}$$

and using a Maxwell relation we have

$$\left. \frac{\partial S}{\partial p} \right|_T = - \left. \frac{\partial V}{\partial T} \right|_p$$

so substituting these into the expression for dH gives

$$dH = C_p dT + \left\{ V - T \left. \frac{\partial V}{\partial T} \right|_p \right\} dp.$$

Now since H is conserved in the throttling process $dH = 0$ so that

$$dT = \frac{1}{C_p} \left\{ T \left. \frac{\partial V}{\partial T} \right|_p - V \right\} dp$$

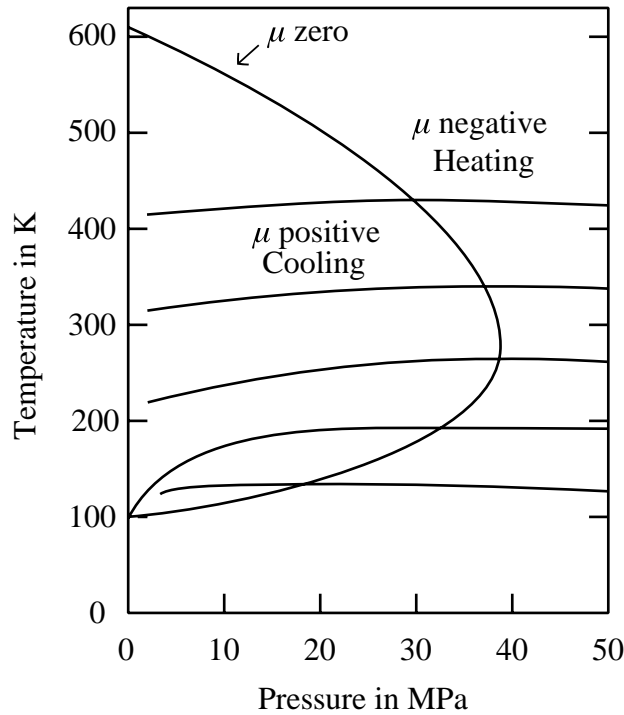
which tells us how the temperature change is determined by the pressure change. The *Joule-Thomson* coefficient μ_J is defined as the derivative

$$\mu_J = \left. \frac{\partial T}{\partial p} \right|_H,$$

giving

$$\mu_J = \frac{1}{C_p} \left\{ T \left. \frac{\partial V}{\partial T} \right|_p - V \right\}$$

This is zero for the ideal gas. When μ is positive then the temperature decreases in a throttling process when a gas is forced through a porous plug.



Isenthalps and inversion curve for nitrogen

3.5.7 Joule-Thomson effect for real and ideal gases

Let us consider a real gas, with an equation of state represented by a virial expansion. We consider the case where the second virial coefficient gives a good approximation to the equation of state. Thus we are assuming that the density is low enough so that the third and higher coefficients can be ignored. This means that the second virial coefficient correction to the ideal gas equation is small and then solving for V in the limit of small $B_2(T)$ gives

$$V = \frac{NkT}{p} + NB_2(T) .$$

so that the Joule-Thomson coefficient is then

$$\mu_J = \frac{NT}{C_p} \left\{ \frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} \right\} .$$

Within the low density approximation it is appropriate to use the ideal gas thermal capacity

$$C_p = \frac{5}{2}Nk$$

so that

$$\mu_J = \frac{2T}{5k} \left\{ \frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} \right\} .$$

3.5.8 Inversion temperature and liquefaction of gases

The inversion curve for nitrogen is shown in the figure. We see that at high temperatures μ_J is negative, and the throttling process leads to heating. As the temperature is decreased the inversion curve is crossed (the inversion temperature T_i) and μ_J becomes positive. For temperatures $T < T_i$ throttling will lead to cooling and this may be used for liquefaction of gases.

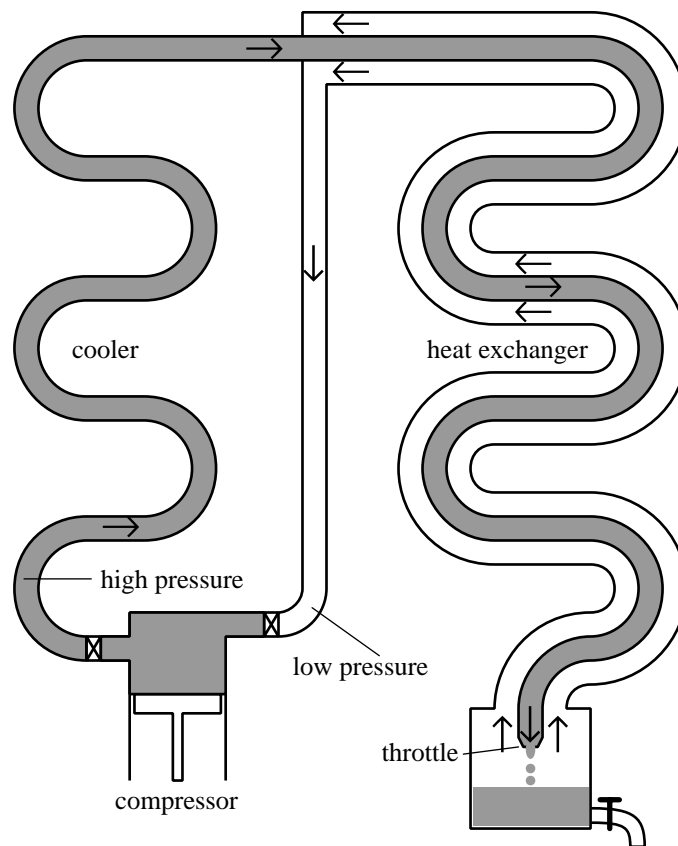
Joule-Kelvin expansion may thus be used to liquefy a gas so long as the temperature starts below the

inversion temperature. For nitrogen $T_i = 621$ K so that room temperature nitrogen will be cooled. However the inversion temperature of helium is 23.6 K, so helium gas must be cooled below this temperature before the Joule-Kelvin process can be used for liquefaction. This may be done by precooling with liquid hydrogen, but that is dangerous. Alternatively free expansion may be used to attain the inversion temperature. In this case helium at a high pressure is initially cooled to 77K with liquid nitrogen. This gas is then expanded to cool below T_i so that throttling can be used for the final stage of cooling.

The inversion temperature is given by the solution of the equation

$$\frac{dB_2(T)}{dT} - \frac{B_2(T)}{T} = 0$$

within the second virial coefficient approximation. Note, however, that this approximation fails to give any pressure dependence of the inversion temperature.



Liquefaction of gas using the Joule-Kelvin effect

End of lecture 17